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THE

PHYSICAL REVIEW.

A STUDY OF THE POLARIZATION OF THE LIGHT EMITTED BY INCANDESCENT SOLID AND LIQUID SURFACES.[1]

By R. A. Millikan.

I.

Introductory.

IN spite of the prodigious activity of physicists during the first three quarters of this century in attacking the problems of reflection, refraction, and polarization in all their different phases, both from the side of experiment and that of mathematical theory, the problem of polarization of light by emission seems to have received comparatively little attention. Although the fact that incandescent solids and liquids emit, at oblique angles of emergence, partially polarized light, was discovered more than seventy years ago, it does not appear even to-day to be very generally known. Few, even of the more complete text-books on physics, make any mention of the fact. Verdet, in his *Optique*, published in 1870, devotes a short paragraph to "Polarization by Emission," in which he says that "there exists upon the subject but a small number of experiments, due mainly to Arago." The summary of these experiments, which he subjoins, reveals none whatever that are quantitative. Since the time of Verdet, no one, so

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far as I am able to discover, has made any careful or elaborate study of the phenomenon with a view to ascertaining its generality, verifying or disproving Arago's assumption as to its cause, or classifying different substances with reference to their power of producing the phenomenon in greater or less degree.

Since even a hasty examination reveals the fact that different substances emit light of widely different percentages of polarization, it appears that a study of the relations of different bodies in this respect ought either to add something to our knowledge of the optical properties of the substances considered, or else, if this particular property is deducible from the already known properties, as Arago assumed it to be, its relation to these properties ought to be definitely proved. This investigation has therefore been undertaken for the purpose, first, of making a somewhat wide range of qualitative experiments upon the nature and generality of the phenomenon; and, secondly, of subjecting Arago's explanation of the cause to the test of comparison with carefully determined experimental quantities.

II.

Historical Review.

The simple facts of polarization of light by emission can best be observed, and in fact were first noticed, upon platinum. If a sheet of that metal be heated to incandescence in the flame of a Bunsen burner, and the emitted light examined by means of a Nicol prism, or any other instrument adapted to the detection of partially polarized light, it will be observed that when the experimenter is viewing the surface normally the emitted light exhibits no trace whatever of polarization, but as the instrument is inclined so as to receive rays emerging obliquely from the surface, the light begins to show evidences of polarization in a plane perpendicular to the plane defined by the normal and the emerging ray. If this plane be called the plane of emission, and the angle included between these two directions *the angle of emission*, the complete phenomenon may be roughly described by

saying that the polarization increases as the angle of emission increases, and becomes, in the case of platinum, exceedingly strong as the emission angle approaches ninety degrees.

The announcement of this fact, and the consequent overthrow of the common belief that light coming immediately from self-luminous bodies is always natural, was made first in 1824 by Arago. In a report made in that year to the Royal Academy of Sciences (see *Annales de Chemie et de Physique* (1) 27, p. 89) he announced that he had some time before made a series of experiments upon the light which emanates from incandescent bodies. "He found that if the bodies are solid or liquid this light is partially polarized by refraction when the rays observed form with the emitting surface an angle of a small number of degrees. As for the light of an ignited gas it presented under no inclination traces of sensible polarization." From these experiments he drew the conclusion "that a considerable portion of the light which enables us to see incandescent bodies is produced in the interior and at depths which are not yet completely determined." "Even when the surface of a solid or liquid was not well polished," Arago still found that he "was able to detect evident traces of polarization." The substances upon which he experimented and from the observation of which he drew his conclusion were only four in number, viz. — solids, wrought iron and platinum; liquids, molten iron and glass (see *Astronomie Populaire*, II., p. 103). He made *no* quantitative measurements, nor even used an instrument which was capable of indicating roughly *amounts* of polarization. His polariscope consisted of a single quartz crystal cut perpendicularly to the optical axis, and a crystal of Iceland spar. The latter produced a double image of an opening in a diaphragm placed just beyond the crystal of quartz. The two images were of course colored when the light was polarized and uncolored when it was natural.

Arago applied the results of his experiment to the determination of the character of the sun's surface. Being unable to detect any trace of polarization in the light emitted by the outer edge of the sun's disk, he drew the well-known conclusion that the surface of the sun can be neither liquid nor solid, but must be gaseous.

After the discovery of the polarization of heat, and the construction of an instrument by Melloni for its detection and measurement, Provostaye and Desain examined the heat rays emitted by luminous platinum and found that they, like the light rays, were polarized in the plane perpendicular to the plane of emergence. Their experiments were few in number and confined entirely to platinum. In 1866 Magnus extended this method of experiment to obscure heat rays, making quantitative measurements upon the heat emitted at the temperature of 100° C., and at an angle of 35°. His experiments embraced the following list of substances: Paraffine, glycerine, white wax, melted calophony, rubol, black glass, transparent glass, quicksilver, aluminium, copper, and tin. For these substances he found a polarization at 35° ranging from 5 per cent to 27 per cent. He drew the conclusion that obscure heat, like light, must undergo refraction in emerging from the surface of the radiating body.

Verdet, in the paragraph upon polarization by emission previously referred to, while stating that little has been done in the investigation of the subject, gives the same explanation of the phenomenon as that first offered by Arago. He says that "it is due to the fact that it is not alone the surface molecules which radiate light; those of the interior layers also radiate, at least to a certain depth; and the rays emitted by the interior molecules undergo refraction at the surface." Since the time of Verdet, I believe no one has made any experiments upon the subject except Violle, who has a brief note in the *Comptes Rendus* of 1887, Vol. 105, p. 111, in which he states that, while making some other experiments upon molten silver, he took occasion to measure the percentages of polarization in the light emitted by that substance at various incidences. He plotted the curve of these percentages and found that it was very well represented by the empirical formula $p_0 = (1 - \cos i)\left(1 + \cos 75° + \frac{i}{5}\right)$, where p_0 represents the ratio of a polarized light to the whole light in the emitted beam, and i the angle of incidence.

Assuming, then, the phenomenon to be due to refraction, he argues that the equality of the amounts of polarization in the

reflected and refracted beams would require that $ep_e = pr_r$, where e is the proportion of the whole light emitted, r the proportion reflected, p_e the proportion of polarized light in the emitted beam, and p_r the proportion of polarized light in the reflected beam. Then, since the whole light is either emitted or reflected, $e+r=1$, and the formula $r=\frac{p_e}{p_e+p_r}$ immediately follows. Taking the experimental values which have been determined for p_r by reflection at ordinary temperatures, he finds that his own results for p_e when substituted in this formula, give a uniformly high reflecting power for molten silver; a result which agrees with the known properties of ordinary polished silver. This forms the nearest approach to a verification of Arago's assumption which has yet been given.

Such is the extent of the work which has thus far been done upon polarization by emission.

III.

Discussion of Arago's Explanation.

The explanation of Arago and Verdet is as yet the only one which has been offered to account for the phenomenon. This explanation does not rest upon careful experimental proof, and, furthermore, there seems to be considerable reason for doubting its correctness. According to that explanation the light which comes to the eye from the *surface* particles is *natural* light; but mixed with this unpolarized light is a quantity of light which has worked its way up from uncertain depths, has undergone reflection and refraction at the surface, and is consequently polarized upon emergence. Aside from the intrinsic difficulty of this conception, the first experiments which were made in this research upon platinum seemed to be inconsistent with such an explanation; for, when a well polished platinum strip was heated to incandescence by means of an electric current and the glowing surface examined by means of a double Wollaston prism, the polarization was found to be so nearly complete for angles in the neighborhood of grazing emergence that one of the images

almost disappeared. But, since platinum is known to be altogether opaque, except in the case of exceedingly thin laminæ, it would seem as though the surface molecules must play a considerable part in the luminosity of the glowing metal; so that, even if the assumption were made that the laws of reflection and refraction would require complete extinction of the ray polarized parallel to the plane of emergence, there still ought to be a considerable amount of light emitted in this plane from the surface molecules; at least, a sufficient quantity to prevent so nearly complete extinction as experiment showed to exist for angles of 88 or 89 degrees.

The only apparent method of reconciling the facts with Arago's explanation was to assume that the opacity of the platinum was greatly diminished by an increase in its temperature. And yet, such experiments as were made to determine whether or not this was the case, gave only negative results. The thinnest sheet of platinum which was capable of being heated to incandescence without melting, was placed in the focus of a powerful beam of light from an arc lantern, the beam having been first polarized by transmission through a Nicol. The plane of the glowing platinum being perpendicular to the beam, the light emerging normally on the other side of the platinum was examined by means of a delicate polariscope. No trace of polarization was detected. Neither could the outlines of the focus be distinguished on the side of the platinum away from the lantern. The sheet of platinum employed was evidently just as opaque as at a lower temperature.

This difficulty of accounting for the extreme polarization noticed at large angles of emergence appeared to be considerably diminished if another cause for the phenomenon were assumed than that given by Arago.

According to the conclusions of Fresnel, Cauchy, Stokes, Mascart and most of the advocates of the elastic solid theory of light, the direction of vibration of the ether particles in plane polarized light is perpendicular to the plane of polarization. It would follow that the light emitted at large angles by platinum vibrates mainly in the direction of the normal to the surface. It is not unnatural to suppose that at the boundary between

very dense and very rare media, like platinum and air, there may be less resistance to vibration in a direction away from the surface than in a direction parallel to the surface, and therefore that the light emitted is composed mainly of vibrations in a direction normal to the surface. If this were the case, the light emitted normally would be unpolarized, while that emitted at oblique angles would be polarized in the plane perpendicular to the plane of emission. Furthermore, the polarization would increase with the angle and might be very great at large angles, in case the difference in density between the two media were very great — conclusions all of which are in accordance with the facts. In view, then, of the inability to account, by Arago's assumption, for the extreme polarization at large angles of emergence, and in view of the plausibility of the other explanation, the following qualitative experiments were made in order to determine with more certainty the nature of the phenomenon.

IV.

Qualitative Experiments.

The object of this part of the research was: —

(1) To make certain that the property of polarization is due to the incandescent body itself, and is not caused by the refraction of the light as it passes through the layers of air of varying density which rest upon the luminous surface; and,

(2) To make observations upon as wide a range of substances as could be made to emit light without combustion, in order to ascertain whether any substance could be found which does not possess the characteristic, and also in order to determine in a general way the relations of different bodies with reference to this property.

For these purposes two instruments were employed; the first, a polariscope similar to that of Arago, save that the simple quartz crystal was replaced by a bi-quartz plate, and the crystal of calc-spar by a double Wollaston prism. This is the same instrument which was afterwards used by Arago in his polarimeter, and it has an advantage over the first form in that the two colors to

be compared are brought into immediate juxtaposition. It is delicate to the extent of detecting a polarization of about 3 per cent (as was shown by succeeding experiments), when white light is under examination. When the light to be tested is monochromatic, as was the case in some of the following experiments, the second form of polariscope was found to be preferable.

In this instrument the bi-quartz is replaced by a cube of glass which has been subjected to strain in cooling. A Nicol also takes the place of the Wollaston prism of the first polariscope. The glass being in the state of strain, is doubly refracting and exhibits with polarized light the familiar dark or light cross which is characteristic of doubly refracting crystals, when cut perpendicularly to the optic axis and viewed by convergent light. With this instrument a polarization of two or three per cent could be easily detected, and it had the further advantage of indicating immediately the azimuth of the plane of polarization. Also, by careful observation of the distinctness of different parts of the figure it was possible, after a small amount of practice, to estimate with considerable correctness the *degree* of polarization.

1. In all experiments which have been previously performed upon this subject, the white-hot body has been in immediate contact with the air. The emitted light was therefore obliged to pass through layers of air of varying density before it reached the eye of the observer. That the light might thus suffer a large number of refractions between the incandescent body and the eye, and so be endowed with the property in question, seemed entirely possible. It was therefore necessary to make some experiment in order to determine whether or not this was the entire or partial cause of the phenomenon. For this purpose the contrivance shown in Fig. 1 was employed. A strip of platinum foil *A* about 4 cm. in length and 5 mm. in width was attached to the platinum and copper wires *B* and *C*. The former was sealed into the glass tube *G*, and the latter was passed through the cork *F* which closed the other end of the tube.

The instrument was first sealed with wax and then connected with the air pump by means of the small tube *D*, and with a strong electric current by means of the wires *B* and *C*. Care

was taken to place the platinum strip as near the axis of the tube as possible, in order that light emitted by it might pass normally through the sides of the tube. Otherwise polarization would have been caused by the passage of the beam through the glass itself. The tube being exhausted until the gauge showed a pressure of only four millimeters, the current was turned on and the glowing strip examined by means of the bi-quartz polari-

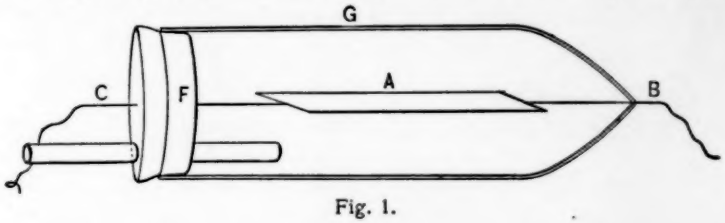

Fig. 1.

scope. The emitted light was still found to be polarized for oblique angles of emergence and did not appear to have undergone any change in intensity. In order, however, to ascertain whether or not the effect of the air was altogether negligible, more delicate experiments were necessary. These will be hereafter described.

2. Having thus proved that the phenomenon is inherent in the body itself, experiments were made upon the following substances with results as indicated: —

SOLIDS. — *Metallic.*

Platinum (polished). — Polarization very strong near grazing emergence, but falling off rapidly as the angle diminishes. Scarcely perceptible at ten degrees.

Silver. — Polarization strong, larger for small incidences than in the case of platinum.

Gold. — Polarization strong; similar to platinum, but apparently less for large angles.

Copper. — Polarization weak, probably due to roughening of surface through oxidization.

Brass. — Polarization weak — (oxidization).

Iron. — Polarization weak — (oxidization).

SOLIDS. — *Non-metallic — transparent.*

Glass. — Polarization weak; imperceptible except at large angles of emergence.

Mica. — Polarization weaker than in glass. Surface roughened by heat.

SOLIDS. — *Non-metallic — opaque.*

Porcelain. — Polarization similar to that produced by glass.

Black Glass. — Polarization similar to that produced by transparent glass.

LIQUIDS.

Molten Silver, " Gold } Polarization similar to that in solid state.

" Iron. — Polarization strong; almost as strong as in molten gold.

" Bronze. — Polarization strong; almost as strong as in molten gold.

Lead. — Polarization weaker than for preceding metals. (Difficult to get a clear surface.)

Zinc. — Polarization weaker than for preceding metals.

From these experiments it will be seen, (1) that the metals show uniformly high percentages of polarization so long as the surface is non-diffusing; (2) that none of the non-metallic substances used produce strong polarization at any angle; (3) that the transparency or opacity of a substance has apparently little effect upon its power of producing polarization in the emitted light; and (4) that any cause which interferes with the perfect smoothness and regularity of the surface destroys in large measure the polarization.

V.

Instrument employed for Quantitative Experiments.

In order to accomplish the second and main object of the research, it became necessary to devise some means of making accurate determinations of the relations of the *constants* of the partially polarized beam. The instrument which has been most employed for such work by previous investigators is the polarimeter of Arago. This is an instrument simple enough in principle, but difficult in construction. Moreover, it does not possess a very high degree of accuracy, owing to the fact that its use depends upon the detection, by means of a bi-quartz polariscope, of the exact point at which all polarization disappears from a beam of light.

Both because of this difficulty of construction and because my own experiments with the bi-quartz polariscope made me distrustful

of the accuracy with which the point of no polarization could be determined, another form of instrument was devised for these experiments which is greatly superior to the Arago polarimeter in simplicity, and is probably more than equal to it in accuracy. The credit of the first conception and use of this method of measuring the constants of partially polarized light is due to Cornu. Violle also used a similar instrument in his determinations upon silver.

In view of the exceeding naturalness and simplicity, as well as the accuracy of the method, it is surprising that it was not earlier discovered and has not been more generally employed. Cornu's description of his instrument was published in '82 in the *Ass'n Française pour l'Avancement des Sciences, Comptes Rendus;* but so far as I can discover, no reference was made to it at the time in any of the scientific journals, nor has it taken its place among other polarimeters in any of the text-books on optics. The instrument as constructed and used for the purposes of these experiments was as follows. A rectangular opening *O*, 1 mm. in width and 2.5 mm. in length, was made in a diaphragm *H* which stood a short distance in front of the double Wollaston prism *A*. The prism was rotated until the extraordinary image of the opening was to the left of the ordinary; the distance of the screen from the prism was then adjusted until the opposite edges of the two images exactly coincided. A Nicol prism *B*, capable of rotating about its axis and furnished with a graduated circle and vernier for reading azimuth to a tenth of a degree, constituted the only other essential part of the instrument. A small telescope *C* was used for viewing the images of the rectangular opening *O*. The instrument was mounted upon a support *G*, furnished with a horizontal axis at *F*, about which the upper portion of the appa-

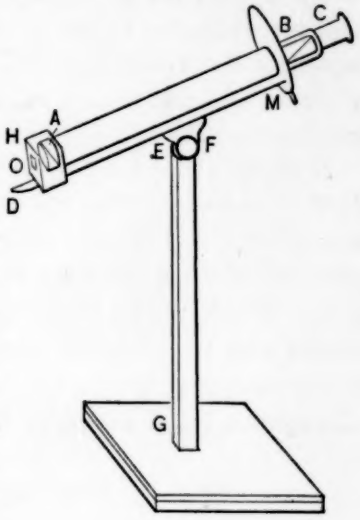

Fig. 2.

ratus could be revolved. The axis of the tube bearing the double prism and Nicol could thus be inclined so as to make any desired angle with the vertical. Since the two images furnished by the double prism consist of light polarized in planes at right angles to each other, the rotation of the Nicol will evidently extinguish each of them in turn. There will be four extinctions in the course of a complete revolution of the Nicol, and between any two extinctions there is a point for which the images, as seen through the Nicol, have exactly equal intensities. If now a partially polarized beam is under examination, and if, the plane of polarization of this beam being known, the principal sections of the prism are set parallel and perpendicular to this plane, that position of the Nicol which equalizes the two images, evidently defines the relation between their original intensities, which is also the relation between the constants of the partially polarized beam.

If we let a and b represent the original amplitudes of vibration in the two images, then the intensities of these images are represented by a^2 and b^2 respectively. The proportion of polarization is evidently the difference between these intensities divided by their sum. If w is the angle which the transmitting plane of the Nicol makes with the direction of vibration of the more intense of the two beams, say a^2, then the intensities of the two images as seen through the Nicol will be by the law of Malus,

$$a^2 \cos^2 w \text{ and } b^2 \sin^2 w. \tag{1}$$

Hence for the position of equality we have,

$$a^2 \cos^2 w = b^2 \sin^2 w \tag{2}$$

or

$$\frac{a^2}{b^2} = \frac{\sin^2 w}{\cos^2 w}. \tag{3}$$

If we call the degree of polarization in the original beam p, we have

$$p = \frac{a^2 - b^2}{a^2 + b^2}; \tag{4}$$

or, from (3),

$$p = \frac{\sin^2 w - \cos^2 w}{\sin^2 w + \cos^2 w} = -\frac{\cos^2 w - \sin^2 w}{1} = -\cos 2w. \qquad (5)$$

Hence, when the position of the Nicol which produces equality in the images has been found, the amount of polarization is immediately given by (5).

Cornu, in discussing the instrument, shows in addition, that, when the principal sections of the partially polarized beam are not known, the degree of polarization may still be found by taking one set of readings in any position whatever of the axes of the double prism, and then rotating the whole instrument through an angle of 90° and taking a second set of readings. The degree of polarization can then easily be shown to be given by the formula

$$p = \sin (w_2 - w_1).$$

In this work, however, we are not concerned with this last formula, since the principal sections were always known.

VI.

Adjustment of the Instrument.

Since the series of experiments here considered were all made upon horizontal surfaces, and since the polarization of the emitted light is always in a plane normal to the surface, but one adjustment of the instrument was necessary, viz. that of bringing the principal sections of the double prism into coincidence with the horizontal and vertical directions.

This adjustment was effected in the following way. The axis of the tube bearing the prism and Nicol was first set, by measurement, parallel to the cross-piece *DM* of the supporting frame. The base *G* was then carefully leveled by means of a common level. The leveling of *DM* then brought the axis of the tube into coincidence with the horizontal line. The telescope was then focussed upon a very fine line of light reflected from the edge of a carefully leveled sheet of white paper placed just in

front of the rectangular opening *O*. Since the line joining the two images produced by a crystal of calc-spar is always parallel to the optical axis of the crystal, it follows, that, when the two images of the horizontal line of light form with each other an unbroken line, the principal sections of the crystal have the desired directions, and the adjustment is perfect. The line of light used in this case was so narrow that the adjustment could be made with great accuracy. This done, the crystal was permanently fastened in position. Thereafter, it was only necessary, before each observation, to level the base of the instrument *G*, in order to bring the principal sections of the crystal into the desired positions.

In order to set the axis of the tube at any desired angle with the vertical, the cross-piece *DM*, parallel to this axis, was leveled, and the angle *DEG*, between the movable arm and the vertical support, was measured by means of a protractor. The zero position being thus determined, any desired inclination could be secured by giving to the angle *DEG* the proper value.

VII.

Degree of Accuracy of the Instrument.

The great sensitiveness of the eye in detecting slight differences in the intensities of images of the same color when brought into close proximity has often been the subject of remark. Cornu claims that the position of equality can be determined with a precision that reaches $\frac{1}{10}$ of a degree. My own observations would not lead me to attribute to the instrument so high a degree of accuracy. Furthermore, these observations are subject to the objection which attaches to all photometric experiments, that the sensitiveness of the eye varies greatly with the physical and mental condition of the observer. At times the extreme difference in my readings for a given set of conditions would be as high as $2\frac{1}{2}$ degrees. Usually, however, the extreme difference was not more than $1\frac{1}{2}$ degrees. For the sake of testing the probable accuracy of the results which are to be given later, several sets of observations were made upon the unpolarized light of a gas flame. The

following illustrate about the average course of the readings. The zero of the instrument not being known, the positions of equality on each side of the positions of extinction were determined: —

Left.	Right.
50.5	39.2
50.0	39.1
50.0	38.7
50.4	38.8
51.3	40.0
50.0	40.0
51.0	40.0
51.1	39.9
50.2	39.2
49.5	39.0
50.4	39.37

$$2w = 89.77$$
$$w = 44.88$$

Since the light from a gas flame is unpolarized, the value of w should have been 45°. The difference is not large, but is slightly greater than the maximum error ascribed to the instrument by Cornu. The above is about an average set of readings. The extreme difference is 1°.8, a difference perhaps slightly greater than that usually found.

A second slight error may sometimes arise in the use of this instrument from the fact that the two images produced by the double prism do not correspond to exactly the same points on the luminous surface. Hence, in order that the results may be correct, it is necessary that the adjoining portions of the incandescent surface be exactly alike. In none of the experiments here recorded were the portions of the luminous surface producing the two images more than 3 mm. apart. Care was always taken to direct the instrument toward a portion of the surface which appeared to be entirely uniform. This error may, I think, be safely disregarded in all of the following cases except one, which will be mentioned later.

A third remark which should be made upon the accuracy of the instrument is that observations for large amounts of polarization are less subject to error than those made upon small amounts. For, since the intensities of the two images compared are propor-

tional to $\sin^2 w$ and $\cos^2 w$, the change in intensity of one of them will be very rapid when w is in the neighborhood either of zero or of 90°. When, however, w is near 45°, the change in intensity corresponding to a small change of angle is comparatively small. Hence, when the polarization is large, and w consequently either large or small, the position of equality can be determined with considerably greater accuracy than when the polarization is weak and w in the vicinity of 45°.

The results obtained for large angles may therefore be considered more trustworthy than the results for small angles.

VIII.

Measurement of the Air Effect.

In the qualitative experiments previously described it was ascertained that the amount of polarization was at least not greatly affected by the contact of the air with the heated surface. Before proceeding to careful quantitative measurements it was necessary to determine whether or not its effect upon the phenomenon is altogether negligible. This could be easily done by means of the polarimeter.

The sealed glass tube containing the platinum strip was again connected with the air-pump, and the air exhausted until the pressure was about 4 mm. The current was turned on, the polarimeter arranged so as to receive the light emitted from the glowing surface at an angle of about 80°, and the Nicol turned until the images were brought into equality. The stop-cock was then suddenly turned and the air admitted. No change whatever could be perceived in the equality of the images. The experiment was repeated a number of times and in a variety of ways, but always with the same result. The conclusion was, that, if the air has any effect whatever upon the proportion of polarization in the beam, that effect is so slight as to be *altogether negligible;* a result exceedingly fortunate for the purposes of this investigation, since, had it been necessary to work upon substances in a vacuum, the following experiments would have been much more difficult, if not altogether impossible.

IX.

Experiments upon Uranium Glass.

The chief difficulties which beset the investigation of polarization by emission are, 1st, the difficulty of obtaining a perfectly *definite* and *regular* incandescent surface with which to work, and 2d, the difficulty of ascertaining with certainty the optical constants of *any* bodies at the temperature of incandescence.

The similarity between a body emitting light by incandescence and a body emitting light by fluorescence was first suggested to me by Professor Rood. According to Tait, the phenomenon of fluorescence is confined mainly to the surface layers. Whatever the cause, then, of polarization by emission, the light coming from a fluorescent surface ought to be polarized in the same way as the light coming from glowing platinum.

Experiment showed this conclusion to be entirely correct. The polarization seen in uranium glass was similar in every respect to that observed in incandescent porcelain, being scarcely discernible at any angle less than 50°, but becoming quite marked between 85° and 90°, and evidently reaching a maximum at grazing emergence.

That this polarization was not due to diffusing particles on the surface was certain for three reasons: 1. The surface was *not* a diffusing surface except to an exceedingly small extent. 2. The light which exhibited the phenomenon of polarization was the characteristic yellowish-green light which uranium emits, and not the blue light which fell upon the surface. 3. The reflecting particles on the surface would have produced a polarization *in* the diffusing plane, *i.e.* in the plane defined by the direction of the beam which entered the instrument and the direction of the incident beam, which was in this case normal to the surface. As a matter of fact, the polarization was perpendicular to this plane.

Here, then, was an instance of polarization by emission in which the surface was perfectly definite and at the same time the optical constants of the substance could be easily and accurately determined.

Accordingly, a careful series of observations was made with the polarimeter. The experiments were all conducted in a well-darkened room, and care was taken not to allow any light to enter the instrument except that emitted by the uranium glass. In order to make the determination of the angles of emission convenient, the light from the lantern was thrown vertically down

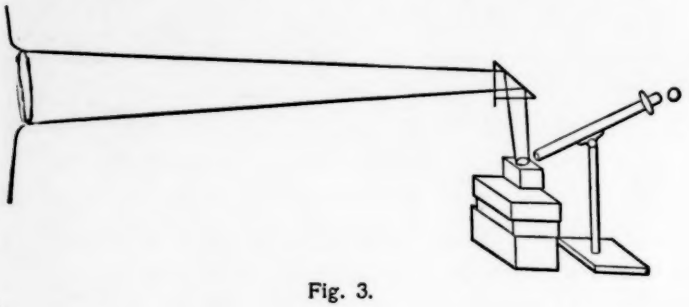

Fig. 3.

upon the surface of the uranium glass by means of total reflection in a right-angled prism. The cube of glass was carefully leveled so that the emitting surface was always horizontal. The arrangement of apparatus is shown in Fig. 3.

Ten readings were taken for every angle of emergence. The results are given in full.

87°.5		85°		80°		75°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
40.5	29.8	42.3	30.7	43.0	32.0	44.5	34.5
39.5	29.9	43.0	31.2	43.3	32.5	45.0	35.0
39.8	28.5	42.5	30.5	43.8	32.3	44.3	35.0
40.0	29.0	41.7	30.9	44.0	32.6	44.5	33.5
39.0	28.9	40.9	31.0	43.3	32.3	44.5	34.4
39.76	29.22	42.1	30.86	43.48	32.34	44.56	34.5
$2w = 68°.98$		$2w = 72°.86$		$2w = 75°.82$		$2w = 79°.06$	
$p = 0.358$		$p = 0.293$		$p = 0.245$		$p = 0.191$	

70°		65°		50°			
Left.	Right.	Left.	Right.	Left.	Right.		
45.5	35 0	47.0	37.0	49.1	38.2		
46.4	36.4	47.2	36.3	48.9	38.2		
46.5	36.5	47.5	37.5	49.0	38.9		
47.0	35.0	48.0	37.0	50.0	39.3		
46.3	36.2	47.4	36.0	49.3	39.0		
46.34	35.8	47.62	36.8	49.26	38.52		
$2w = 82°.1$		$2w = 84°.4$		$2w = 87°.78$			
$p = 0\ .139$		$p = 0\ .098$		$p = 0\ .039$			

The chief difficulty encountered in making these determinations was the lack of perfect uniformity in the emitting surface. The uranium glass, being rendered self-luminous by the beam from the lantern, could not have entire uniformity over its surface unless the illuminating beam was uniform in intensity, which was not the case. The images corresponded to points on the surface not more than 2 mm. apart, and yet it was found that the equality of the images could be sometimes disturbed by directing the instrument toward a new portion of the field. As great care as possible was taken to direct the polarimeter toward such portions of the field as appeared to have a uniform illumination, and it is not thought that the error due to this cause could have been great.

Phosphorescent bodies were also examined for polarization, but the light emitted by such bodies is so weak that no definite results were obtained.

[*To be continued.*]

ALTERNATING CURRENTS WHEN THE ELECTROMOTIVE FORCE IS OF A ZIGZAG WAVE TYPE.

BY E. C. RIMINGTON.

ALTHOUGH no alternate-current dynamo will give an electromotive force of a zigzag form, still with some commercial machines, the electromotive force may be nearer to this type than to a sine curve, so that it is useful to investigate the current in the limiting case of a pure zigzag electromotive force.

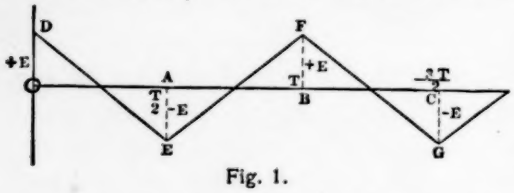

Fig. 1.

Figure 1 represents a wave of this type. It is composed of the broken straight lines *DE*, *EF*, *FG*, all of equal length and equally inclined to the horizontal axis. *OB* will represent the periodic time *T*, and *OD* the maximum value of the electromotive force or *E*.

The equation to these lines will be

$$e = \pm E\left(1 - \frac{4}{T}t\right),$$

the plus sign being employed when they slope downwards, as *DE* and *FG*, and the minus sign when they slope upwards, as *EF*.

The time t must always be reckoned from a point of maximum or minimum electromotive force, such as *O*, *A*, *B*, or *C*, and must be between the limits *O* and $\frac{T}{2}$.

Of course an electromotive force of this form could be expressed as a function of time continuously reckoned onwards from some zero point by means of a Fourier sine series, and the current equation obtained as a sum of terms, of which one is contributed by each of the terms in the Fourier series. This method does

not lead to satisfactory results, and the better one to follow in this case is what may be called the "piecemeal" method. The manner in which it is to be carried out may be sketched shortly thus. We must presuppose some initial condition. The one here taken is that the electromotive force has been acting steadily, and the current has attained a steady value. Obtain now the current equation for the portion of the electromotive force zigzag DE, and assuming the initial current at D to be $\frac{E}{R}$, find the final current at E, *i.e.* the current when time equals $\frac{T}{2}$. This will be the initial current for the second half period or the portion EF; we can thus find the final current or current corresponding to point F. By a similar way of procedure, the current at the end of each half period can be found, and it will be seen that a single law is followed so that the current at the end of any half-period (*i.e.* when the electromotive force is a maximum or a minimum), after an indefinitely long time has elapsed, can be found, and this will be independent of the assumed initial condition. Remembering that the current at the end of a half period is obviously the same as the initial current of the next half period, we can now obtain the current equation for any time t, during a half period, t being reckoned from its commencement. This is the method of treatment that will be employed in the following. Many of the steps in the mathematical working are omitted on account of length, but enough have been put in to make clear the method employed.

Suppose that the electromotive force $+E$ has been acting before the time denoted by the point O in the diagram, and that the current has the steady value $\frac{E}{R}$. Let R be the resistance and L the self-inductance of the circuit. Then the current equation is

$$e = CR + L\frac{dC}{dt},$$

and consequently for the portion such as DE on the diagram,

$$E\left(1 - \frac{4}{T}t\right) = CR + L\frac{dC}{dt}.$$

This is an equation of the well-known type

$$\frac{dy}{dx}+Py=Q,$$

where P and Q are functions of x only. Its solution is

$$y=e^{-\int Pdx}\left\{\int e^{\int Pdx}Qdx+k\right\},$$

where k is a constant and $e=2.718\ldots$.

Hence

$$C=e^{-\frac{R}{L}t}\left\{\frac{E}{L}\int e^{\frac{R}{L}t}\left(1-\frac{4}{T}t\right)dt+k\right\}$$

$$=\frac{E}{R}\left\{1-\frac{4}{T}\left(t-\frac{L}{R}\right)\right\}+ke^{-\frac{R}{L}t}, \qquad (1)$$

when the electromotive force is diminishing.

And similarly

$$C=-\frac{E}{R}\left\{1-\frac{4}{T}\left(t-\frac{L}{R}\right)\right\}+k'e^{-\frac{R}{L}t}, \qquad (2)$$

when the electromotive force is increasing.

Now consider the portion of electromotive force wave represented by DE.

When $t=0$, $C=\frac{E}{R}$ by assumption. Hence, substituting these values in (1),

$$k=-\frac{4EL}{R^2T}$$

Call, for shortness, $\frac{RT}{2L}=n$, or $n=$the half-period $\left(\frac{T}{2}\right)$ divided by the time constant of the circuit $\left(\frac{L}{R}\right)$.

Then we may write

$$C=\frac{E}{R}\left(1-\frac{4}{T}t+\frac{2}{n}-\frac{2}{n}e^{-\frac{R}{L}t}\right).$$

Again, when $t=\frac{T}{2}$,

$$C_{\frac{T}{2}}=\frac{E}{R}\left\{\frac{2}{n}(1-e^{-n})-1\right\}=-\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})\right\}.$$

Now the current at the end of the first half-period is obviously the same thing as the current at the beginning of the second half-period. Hence, making $t=0$ in equation (2), we have

$$\frac{E}{R}\left\{\frac{2}{n}(1-e^{-n})-1\right\}=-\frac{E}{R}\left(1+\frac{2}{n}\right)+k',$$

or

$$k'=\frac{E}{R}\cdot\frac{2}{n}(2-e^{-n}).$$

Substituting this value in (2), and making $t=\frac{T}{2}$, gives the current at the end of the second half-period; or

$$C_{\frac{T}{2}}=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})^2\right\}=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n})\right\}.$$

Proceeding in a similar manner for the third half-period, it will be found that

$$k=-\frac{E}{R}\cdot\frac{2}{n}\{1+(1-e^{-n})^2\};$$

and

$$C_{\frac{T}{2}}=-\frac{E}{R}\left[1-\frac{2}{n}\{(1-e^{-n})\{1-e^{-n}(1-e^{-n})\}\}\right].$$

In the same way the current at the end of the fourth half-period is

$$C_{\frac{T}{2}}=\frac{E}{R}\left[1-\frac{2}{n}[(1-e^{-n})\{1-e^{-n}(1-e^{-n}\overline{1-e^{-n}})\}]\right]$$

$$=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n}+e^{-2n}-e^{-3n})\right\},$$

and so on. Hence the current at the end of a half-period after the zigzag electromotive force has been acting for a considerable period of time will be

$$C_{\frac{T}{2}}=\pm\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n}+e^{-2n}-e^{-3n}+e^{-4n}-,\text{ etc.})\right\}.$$

Now the series $1-e^{-n}+e^{-2n}-e^{-3n}+$ etc. is a geometrical progression whose constant factor is $-e^{-n}$, and this is fractional; hence its sum equals $\frac{1}{1+e^{-n}}$

Therefore $$C_{\frac{T}{2}}=\pm\frac{E}{R}\left(1-\frac{2}{n}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right)=\pm\frac{E}{R}\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right], \qquad (3)$$

the latter expression being obtained from the fact that

$$\frac{1-e^{2n}}{1+e^{2n}}=-\tanh n.$$

The + sign is used if during the half-period under consideration the electromotive force has been increasing, and the − sign if decreasing.

Taking equation (1), and making $t=0$, we have, by the aid of (3),

$$\frac{E}{R}\left(1-\frac{2}{n}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right)=\frac{E}{R}\left(1+\frac{2}{n}\right)+k;$$

or $$k=-\frac{E}{R}\cdot\frac{2}{n}\left(1+\frac{1-e^{-n}}{1+e^{-n}}\right)=-\frac{E}{R}\cdot\frac{4}{n}\cdot\frac{1}{1+e^{-n}}.$$

Hence (1) becomes

$$C=\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right\}.$$

Similarly, (2) will become

$$C=-\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}\cdot t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right\}.$$

Hence we may write

$$\begin{aligned}C&=\pm\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right\}\\&=\pm\frac{E}{R}\left\{1+\frac{2}{n}(1-y)-\frac{4}{n}\cdot\frac{\cosh y-\sinh y}{1+\cosh n-\sinh n}\right\}; \qquad (4)\end{aligned}$$

where $$n=\frac{\frac{T}{2}}{\frac{L}{R}}=\frac{RT}{2L}, \text{ and } y=\frac{R}{L}t,$$

since $e^{-n}=\cosh n-\sinh n$.

The + sign is to be taken when t is reckoned from the time of a + maximum of electromotive force, and the − sign when reckoned from a − maximum.

To find the time at which the current is a maximum or minimum, and its value.

Differentiating (4) with respect to time, and equating to zero, gives

$$-\frac{4}{T}+\frac{4R}{Ln}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}=0;$$

or,

$$t=\frac{L}{R}\log_e\frac{2}{1+e^{-n}}. \qquad (5)$$

If t be reckoned from a maximum of electromotive force, the current will be a maximum; if from a minimum of electromotive force, a minimum. The term $\frac{L}{R}\log_e\frac{2}{1+e^{-n}}$ evidently represents the time lag of the maximum and minimum values of the current, behind those of the electromotive force, respectively.

Substituting the above value for t in equation (4), we obtain

$$C_{\max.}=\frac{E}{R}\left\{1+\frac{2}{n}-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}-\frac{4}{n(1+e^{-n})}\cdot\frac{1}{e^{\log_e\frac{2}{1+e^{-n}}}}\right\}$$

$$=\frac{E}{R}\left\{1-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}\right\}. \qquad (6)$$

$\frac{R}{1-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}}$ may be called the impedance of the circuit, and is a function of R, L, and T. Thus we have the maximum current equal to the maximum electromotive force divided by the impedance, in an analogous manner to the case of a sine function electromotive force, in which the impedance $=R\sqrt{1+\frac{4\pi^2L^2}{T^2R^2}}$, and is a function of R, L, and T.

Again, from equation (4),

$$\frac{dC}{dt}=\frac{E}{R}\left(\frac{4R}{Ln}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}-\frac{4}{T}\right);$$

and

$$\frac{d^2C}{dt^2}=-\frac{4ER}{nL^2}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}$$

Now these values apply to a half-period, during which the electromotive force is diminishing, since the + sign has been taken in (4). The current increases until

$$t=\frac{L}{R}\log_e\frac{2}{1+e^{-n}},$$

and then decreases. Hence $\frac{dC}{dt}$ is first positive and then becomes negative; $\frac{d^2C}{dt^2}$ is always negative. This means that the rate of change of current is greatest when $t=0$ and $t=\frac{T}{2}$; that is, at the times when the electromotive force has its maxima and minima.

From equation (4) it is seen that the current is zero when

$$\frac{4}{T}t+\frac{4}{n}\cdot\frac{1}{1+e^{-n}}\,e^{-\frac{R}{L}t}=1+\frac{2}{n},$$

but unfortunately this equation does not admit of a general solution.

To find the virtual current.

By the virtual current is meant the square root of the mean square value. It is found by squaring equation (4), multiplying by dt, integrating between the limits $\frac{T}{2}$ and 0, then dividing by $\frac{T}{2}$, and taking the square root.

Squaring (4) gives

$$\frac{E^2}{R^2}\Big[\Big(1+\frac{2}{n}\Big)^2+\frac{16}{T^2}t^2-\frac{8}{T}\Big(1+\frac{2}{n}\Big)t+\frac{16}{n^2}\cdot\frac{e^{-\frac{2R}{L}t}}{(1+e^{-n})^2}$$
$$-\frac{8}{n}\Big(1+\frac{2}{n}\Big)\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}+\frac{32}{nT}\cdot\frac{1}{1+e^{-n}}\cdot te^{-\frac{R}{L}t}\Big].$$

Multiplying by dt and integrating between limits $\frac{T}{2}$ and 0, we have

$$\frac{E^2}{R^2}\Big[\Big(1+\frac{2}{n}\Big)^2\frac{T}{2}+\frac{16}{T^2}\cdot\frac{T^3}{24}-\frac{8}{T}\Big(1+\frac{2}{n}\Big)\frac{T^2}{8}-\frac{16}{n^2}\cdot\frac{L}{2R}\cdot\frac{e^{-2n}-1}{(1+e^{-n})^2}$$
$$+\frac{8}{n}\Big(1+\frac{2}{n}\Big)\cdot\frac{e^{-n}-1}{1+e^{-n}}\cdot\frac{L}{R}-\frac{32}{nT}\cdot\frac{L}{R}\cdot\frac{1}{1+e^{-n}}\Big\{\frac{T}{2}e^{-n}-\frac{L}{R}\Big(1-e^{-n}\Big)\Big\}\Big]$$

Dividing by $\frac{T}{2}$ and simplifying, this becomes

$$\frac{E^2}{R^2}\left\{\frac{1}{3}-\frac{4}{n^2}+\frac{8}{n^3}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right\}=\frac{E^2}{R^2}\left\{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]\right\}.$$

Hence the virtual current is

$$C_v=\frac{E}{R}\sqrt{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left(1-\frac{2}{n}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right)}=\frac{E}{R}\sqrt{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]}. \quad (7)$$

As an example, take a circuit whose resistance $R=1$ ohm, self-inductance $L=.01$ henry, in which the maximum electromotive force, or $E=20$ volts, and the frequency $=100$, or periodic time $T=.01$ second. Then $n=\frac{RT}{2L}=\frac{1}{2}$

Equation (4) then becomes

$$C=\pm 100\left(1-.8y-.995936\cdot\frac{1}{e^y}\right),$$

where $y=\frac{R}{L}t=100t$; or

$$C=\pm 100\{1-.8y-.995936\ (\cosh y-\sinh y)\}.$$

The latter is the more convenient form for the purposes of calculation, as a very good set of tables of values of $\cosh\theta$ and $\sinh\theta$ for values of θ from .01 to 4 at intervals of .01 has been published by the Physical Society of London, the working out being due to Mr. Blakesley.

From equation (5) it is found that the value of y for maximum current is .2191, and the maximum current from (6) is 2.474 amperes.

The following table has been worked out for values of y differing by .05, for a half-period, during which the electromotive force diminishes from $+20$ to -20. Obviously for the next half-period, during which the electromotive force will increase from

-20 to $+20$, the values of the current will be the same with their signs changed, as will be seen from equation (4).

t	y	Current in amperes.	Remarks.
0.0	0.0	+0.406	Rate of increase a maximum.
0.0005	0.05	+1.264	
0.001	0.1	+1.884	
0.0015	0.15	+2.279	
0.002	0.2	+2.460	
0.002191	0.2191	+2.474	Maximum current.
0.0025	0.25	+2.436	
0.003	0.3	+2.219	
0.0035	0.35	+1.818	
0.004	0.4	+1.240	
0.0045	0.45	+0.496	
0.005	0.5	−0.406	Rate of decrease a maximum.

The maximum current = 2.474. The virtual current = 1.798 from equation (7).

With a sine function electromotive force having a maximum value of 20 volts,

the maximum current = 3.145,
the virtual current = 2.223.

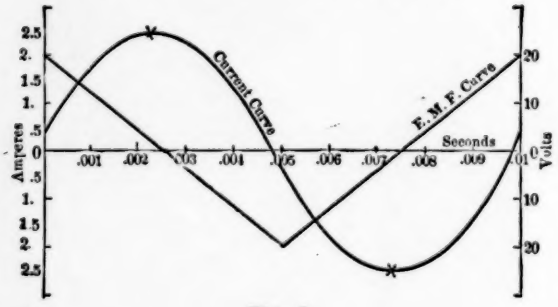

Fig. 2.

E. M. F. and current curves for one complete period. $E = 20$ volts; $R = 1$ ohm; $L = .01$ heavy; $T = .01$ sec.; frequency = 100; max. current = 2.478; virtual current = 1.8.

Figure 2 shows these results plotted as a curve, the scale of volts being one-tenth that of amperes. The points of maximum and minimum current are marked with crosses. It will be noticed that in this particular circuit the current curve is not very unlike

a sine curve in appearance. With less self-inductance, however, it will become more pointed, as evidently in the limiting case of no self-inductance, it must coincide in shape with the curve of electromotive force.

To find the mean power.

The electromotive force at any instant when decreasing is

$$e=E\left(1-\frac{4}{T}t\right),$$

and the corresponding current

$$C=\frac{E}{R}\left(1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right).$$

Hence the power at any instant is

$$P=eC=\frac{E^2}{R}\left(1-\frac{4}{T}t\right)\left(1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right).$$

Multiplying by dt, and integrating between limits $\frac{T}{2}$ and 0 gives

$$\int_0^{\frac{T}{2}}Pdt=\frac{E^2}{R}\left\{-\frac{T}{2}+\frac{2}{3}T+\frac{4}{n}\cdot\frac{L}{R}\cdot\frac{e^{-n}-1}{1+e^{-n}}\right.$$
$$\left.-\frac{16}{n}\cdot\frac{L}{RT}\left\{\frac{T}{2}e^{-n}-\frac{L}{R}(1-e^{-n})\right\}\right\}.$$

Now mean power or

$$P=\frac{\int_0^{\frac{T}{2}}Pdt}{\frac{T}{2}}=\frac{E^2}{R}\left\{\frac{1}{3}-\frac{4}{n^2}+\frac{8}{n^3}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right\}$$

$$=\frac{E^2}{R}\left\{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]\right\}. \qquad (8)$$

This result is, of course, equal to the virtual current squared and multiplied by R.

We may also write P_m in the form

$$P_m = EC_{max.} \cdot \frac{\frac{1}{3} - \left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n} \cdot \tanh \frac{n}{2}\right)}{1 - \frac{2}{n} \log_e \frac{2}{1+e^{-n}}}.$$

Again, since $e = E\left(1 - \frac{4}{T}t\right)$, the virtual electromotive force, or

$$E_v = \sqrt{\frac{\int_0^{\frac{T}{2}} e^2 dt}{\frac{T}{2}}} = \frac{E}{\sqrt{3}}; \text{ and } C_v = \frac{E}{R}\sqrt{\frac{1}{3} - \left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n}\tanh \frac{n}{2}\right)}.$$

Hence P_m may be written

$$P_m = E_v C_v \sqrt{1 - 3\left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n}\tanh \frac{n}{2}\right)}.$$

It is interesting to consider the other limit of wave-type of an alternating dynamo, viz. the rectangular wave-type as shown in Fig. 3. This is the case of a constant electromotive force periodically reversed, and its investigation is considerably simpler than the foregoing one. It can, however, be treated in a precisely similar manner, and the results obtained are that the current at the end of a half-period reckoned from the instant of reversal of electromotive force is

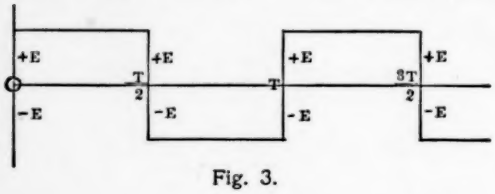

Fig. 3.

$$C_{\frac{T}{2}} = \pm \frac{E}{R} \cdot \frac{1 - e^{-n}}{1 + e^{-n}} = \pm \frac{E}{R} \tanh \frac{n}{2} \qquad (9)$$

Here n has the same meaning as before, viz. $\frac{\frac{T}{2}}{\frac{L}{R}}$; the + sign is to be taken when the reversal has been from a negative value of the electromotive force to a positive one, and *vice versâ*.

We also obtain

$$C=\pm\frac{E}{R}\left(1-\frac{2}{1+e^{-n}}\cdot e^{-\frac{R}{L}t}\right)$$

$$=\pm\frac{E}{R}\left\{1-\frac{2(\cosh y-\sinh y)}{1+\cosh n-\sinh n}\right\}, \qquad (10)$$

where y, as before, equals $\frac{R}{L}t$.

The current is zero when

$$\frac{2}{1+e^{-n}}e^{-\frac{R}{L}t}=1,$$

or when

$$t=\frac{L}{R}\log e\frac{2}{1+e^{-n}},$$

the same value of t that made the current a maximum or minimum in the case of the zigzag electromotive force. There is no mathematical maximum or minimum for the current, but obviously from (10) it is greatest or least when $t=\frac{T}{2}$, that is, at the moments of reversal, or,

$$C_{max.}=C_{\frac{T}{2}}=\frac{E}{R}\cdot\frac{1-e^{-n}}{1+e^{-n}}=\frac{E}{R}\tanh\frac{n}{2}$$

The virtual current, or

$$C_v=\frac{E}{R}\sqrt{\left\{1-\frac{2}{n}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right\}}=\frac{E}{R}\sqrt{1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}} \qquad (11)$$

The formula given in (11) has been published by Mr. Kennelly in the *Electrical World*, Nov. 11, 1893, page 397, where, however, it is misprinted as $\frac{E}{R}\sqrt{\frac{\tanh\frac{n}{2}}{1-\frac{n}{2}}}$

The mean power or P_m will obviously be

$$P_m=C_v^2R=\frac{E^2}{R}\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right].$$

The following table has been calculated from equation (10) for the same circuit as considered previously. With numerical values substituted, (10) becomes

$$c = \pm 20\{1 - 1.24492(\cosh y - \sinh y)\},$$

and

$$y = \frac{R}{L}t = 100\,t.$$

t	y	Current in amperes.	Remarks.
0.0	0.0	−4.898	Current a minimum.
0.0005	0.05	−3.684	
0.001	0.1	−2.528	
0.0015	0.15	−1.430	
0.002	0.2	−0.3850	
0.002191	0.2191	0.0	Current zero.
0.0025	0.25	+0.6082	
0.003	0.3	+1.555	
0.0035	0.35	+2.454	
0.004	0.4	+3.310	
0.0045	0.45	+4.124	
0.005	0.5	+4.898	Current a maximum.

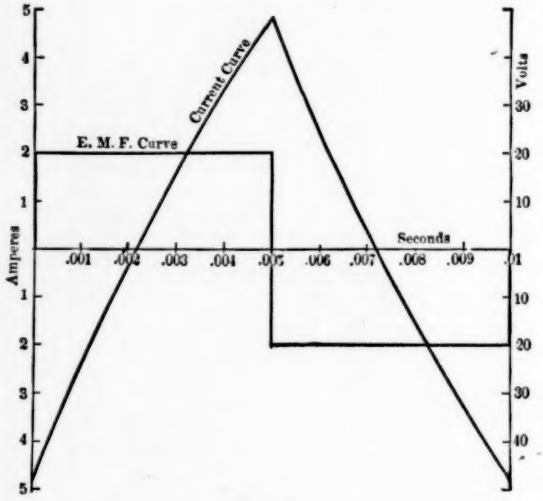

Fig. 4.

E. M. F. and current curves for one complete period. $E = 20$ volts; $R = 1$ ohm; $L = .01$ heavy; $T = .01$ sec.; frequency = 100; max. current = 4.898; virtual current = 2.851.

The maximum current = 4.898,
the virtual current = 2.851 from (11).

For the zigzag electromotive force the values were

maximum current = 2.474,
virtual current = 1.798.

For a sine electromotive force

maximum current = 3.145,
virtual current = 2.223.

Figure 4 gives the above results plotted on the same scale as in Fig. 2, the scale of volts being one-tenth those of the amperes.

It will be seen that with a sinusoidal electromotive force, the maximum and virtual currents have values which lie between those of the two extreme cases of rectangular and zigzag electromotive forces.

ON TERNARY MIXTURES. II.

BY WILDER D. BANCROFT.

THE formula $x^{\alpha}y^{\beta}=$Constant, which was found to express the condition for equilibrium in a saturated ternary solution,[1] is not wholly satisfactory, since it contains no term expressing the variation of the consolute liquid in case one of the non-miscible liquids is kept constant, and also because a change in the units in which x and y are expressed or a change in the amount of the consolute liquid taken affects the constant of the formula. This can be remedied by the following reasoning. According to Gibbs and to experiment, the absolute mass of a phase has no effect on the equilibrium. Therefore increasing the quantities of x and y m-fold involves increasing the quantity of the consolute liquid m-fold if the solutions are to remain at the saturation point. This would increase the value of the constant $m^{\alpha+\beta}$ times. If then x and y denote the values in cubic centimeters of the non-miscible liquids A and B, z the corresponding value for the consolute liquid S, we have as equation of equilibrium for saturated solutions the expression:—

I. $$\frac{x^{\alpha}y^{\beta}}{z^{\alpha+\beta}}=C.$$

If, as was done, z is kept constant, this simplifies to formula (4), which I will renumber I*a*.:—

I*a*. $$x^{\alpha}y^{\beta}=C_1.$$

If y is constant, x and z varying, we have:—

I*b*. $$\frac{x^{\alpha}}{z^{\alpha+\beta}}=C_2.$$

[1] PHYSICAL REVIEW, Vol. III., No. 1.

And if x is constant, y and z varying, we have:—

Ic. $$\frac{y^{\beta}}{z^{\alpha+\beta}}=C_3.$$

In Equation I., the value of C is a function of the nature of the units in which x, y, and z are expressed; but independent of the size. Thus grams and kilograms give the same result, cubic centimeters and liters; but the weight constant is different from the volume constant, and the constants for reacting weights or reacting volumes would have still other values. C is also dependent on the absolute value of the exponential factors α and β. We can, however, eliminate this effect by writing

(6) $$C=K^{\alpha+\beta},$$

in which case K remains entirely unchanged, when we substitute $\frac{\alpha}{\beta}=n$. In Table VII. I give in the first two columns the values for log C according to the general formula $\frac{x^n y}{z^{n+1}}=C$, when x, y, and z are expressed in volumes. Since $z=5$ in all these measurements, Table VII. gives the constants of the preceding tables less the corresponding values of $(n+1)$ log 5. It would have been better to calculate the integration constant using the rational exponents α and β; but only their ratio can be determined by a study of equilibrium in one liquid layer, and the case of two liquid layers will form the subject of a separate communication. In columns three and four are the corresponding values of K_1 and K_2 according to Equation (6). They are the constants of the preceding two columns divided by the appropriate values of $n+1$.

TABLE VII.

Mixtures.	log C_1.	log C_2.	log K_1.	log K_2.
H_2O, $CHCl_3$, C_2H_5OH . . .	$\bar{1}.163$	$\bar{1}.266$	$\bar{1}.711$	$\bar{1}.652$
H_2O, $CHCl_3$, CH_3OH . . .	$\bar{2}.984$	$\bar{1}.489$	$\bar{1}.692$	$\bar{1}.773$
H_2O, $CHCl_3$, CH_3COCH_3 . .	$\bar{2}.506$	....	$\bar{1}.381$	....
H_2O, C_6H_6, C_2H_5OH . . .	$\bar{2}.737$	$\bar{2}.737$	$\bar{1}.514$	$\bar{1}.514$
H_2O, C_6H_6, CH_3OH . . .	$\bar{2}.482$	$\bar{2}.184$	$\bar{1}.388$	$\bar{1}.395$
H_2O, C_6H_6, CH_3COCH_3 . . .	$\bar{2}.584$	$\bar{2}.471$	$\bar{1}.410$	$\bar{1}.349$

The values given under x and y in Tables I.–VI. are amounts of the liquids A and B in a given quantity of S, — in this case 5 c.c. A glance at the tables will show that these figures are very far from expressing volume concentrations, *i.e.* quantity of substance in a given volume of the solution. As most theoretical generalizations in chemistry are expressed in volume concentrations, it will be necessary to see what effect such a change would have on general Formula I. If there is no contraction or expansion on mixing, the volume of the solution will be the sum of the component volumes, or $V=x+y+z$, and the volume concentrations will be $\frac{x}{x+y+z}$, $\frac{y}{x+y+z}$, $\frac{z}{x+y+z}$, respectively. This simple case may be said never to occur, and the volume of the solution is an at present unknown function of the component volumes represented by the expression $V=F(x, y, z)$. While the knowledge of the form of this function is necessary to enable us to calculate the volume concentrations of a given solution from our experimental data, it is superfluous in the present discussion. We have (from Formula I.): —

$$\alpha \log x+\beta \log y-(\alpha+\beta) \log z=\log C.$$

Now $$\alpha \log V+\beta \log V-(\alpha+\beta) \log V=0;$$

$$\therefore \alpha \log \frac{x}{V}+\beta \log \frac{y}{V}-(\alpha+\beta) \log \frac{z}{V}=\log C;$$

or $\frac{x^{\alpha}y^{\beta}}{z^{\alpha+\beta}}=C$, if x, y, and z denote volume concentrations instead of having their previous significance. Since α, β, and C remain unchanged, we find that Equation I. represents the series of saturated solutions obtained at constant temperature with any two non-miscible liquids, and a third liquid miscible in all proportions with each of the other two, provided no chemical reaction takes place, and provided the reacting weights of the liquids remain unchanged. It is immaterial whether x, y, and z denote volume concentrations, or concentrations of two of the substances in a constant quantity of the third.

As has been said, volume concentrations are generally looked upon as the only scientific way of expressing data. This is per-

fectly natural when we remember that our theoretical ideas have been formed almost entirely upon a study of the gaseous state. It is not a necessary method, and in this particular case it is decidedly disadvantageous, practically to use volume concentrations. It involves a determination of the density of each solution, increasing the work and bringing in a new source of error. When expressed in volume concentrations, all three components vary, and while it is a simple matter to plot three variables in a plane,[1] I know of no way in which this can be done for the logarithms of these variables. By the method which I have followed, one constituent can be kept constant, no density determinations are necessary, and there are only two variables. The formula being hyperbolic, by plotting the data on logarithmic coördinates one gets a straight line, any variation from which is easily seen, while the constants of the curve can be determined from the diagram with more speed and accuracy than by substituting the experimental values in an equation and solving for two unknown quantities.

The next case to be considered is when we have two partially miscible liquids, and a third miscible in all proportions with each of the others. Formula I. cannot apply here, because it was deduced for two non-miscible liquids, and this condition is no longer fulfilled. There are two ways of treating a problem like this. One is to change the conditions of the experiment until they agree with the formula; the other is to change the formula till it conforms to the conditions of the experiment. I have done both. I will suppose, for the sake of clearness, that the two partially miscible liquids are ether and water. Saturated solutions of water in ether are absolutely non-miscible at the temperature for which they are saturated, being thus an improvement over benzol and water, which are slightly miscible theoretically. If x and y in Equation I*a* mean quantities of saturated water and saturated ether solutions, instead of pure water and pure ether, the conditions are satisfied for which this formula was deduced, and the equation must apply. I have found that it did, and the experimental proof is given in Tables IX. and XI.

[1] Gibbs, Thermodynamische Studien, p. 141; Roozeboom, Zeitschr. f. ph. Chem., XII. 369. 1893.

This being settled, we can attack the second part of the problem. Let X denote cubic centimeters of saturated solution of ether in water, Y cubic centimeters of saturated solution of water in ether which saturate a given quantity of a consolute liquid. It is found experimentally that

(7) $$X^{\alpha}Y^{\beta}=\text{Constant},$$

or, if we set $\frac{\alpha}{\beta}=n$, we shall have

(8) $$X^{n}Y=C.$$

If s_1 is the solubility of ether in water, s_2 the solubility of water in ether, both expressed in volumes per cubic centimeter of the solvent synthetically, we shall have, if no contraction or expansion takes place in forming the saturated solutions of water in ether and ether in water:—

(9) $$X=A+s_1A\,;\quad Y=B+s_2B\,;$$

(10) $$(A+s_1A)^{n}(B+s_2B)=C\,;$$

where A=c.c. water in X, B=c.c. ether in Y. As we must assume some contraction or expansion, let the ratio of the actual volume to the sum of the component volumes be σ_1 in the saturated solution of ether in water, and σ_2 in the saturated solution of water in ether. We have then:—

(11) $$X=\sigma_1(A+s_1A)\,;\quad Y=\sigma_2(B+s_2B)\,;$$

(12) $$\{\sigma_1(A+s_1A)\}^{n}\{\sigma_2(B+s_2B)\}=C_1\,;$$

which can be rewritten:—

(13) $$(A+s_1A)^{n}(B+s_2B)=\frac{C_1}{\sigma_1{}^{n}\sigma_2}.$$

If x and y denote cubic centimeters of pure water and pure ether dissolved in a given quantity of the consolute liquid, we have:—

(14) $$x=A+s_2B\,;\quad y=B+s_1A.$$

Solving for A and B:—

(15) $$A=\frac{x-s_2y}{1-s_1s_2}\,;\quad B=\frac{y-s_1x}{1-s_1s_2}$$

Substituting these values in (13):—

$$(16) \qquad \left\{ \frac{1+s_1}{1-s_1s_2}(x-s_2y) \right\}^n \left\{ \frac{1+s_2}{1-s_1s_2}(y-s_1x) \right\} = \frac{C_1}{\sigma_1{}^n\sigma_2}.$$

Since σ_1, σ_2, s_1, s_2, are constants for constant temperature, we can simplify equation (16) into:—

$$(17) \qquad (x-s_2y)^n(y-s_1x) = C_2,$$

where the relation between C_1 and C_2 is

$$(18) \qquad \frac{C_1}{C_2} = \frac{\sigma_1{}^n\sigma_2(1+s_1)\ (1+s_2)}{(1-s_1s_2)^{n+1}}.$$

Eliminating the effect due to the arbitrary quantity of consolute liquid used, we have:—

$$(19) \qquad \frac{(x-s_2y)^n(y-s_1x)}{z^{n+1}} = C_3;$$

where $C_3 = \frac{C_2}{z^{n+1}}$. Reverting to the most general form, so as to make the equation correspond in form to Equation I.,

$$\text{II.} \qquad \frac{(x-s_2y)^\alpha(y-s_1x)^\beta}{z^{\alpha+\beta}} = C.$$

Equation II. is more general than Equation I., the latter being merely a special case of the former, where the terms representing the mutual solubilities are so small that they can be neglected.

In testing these equations I took, as pairs of partially miscible liquids, ether and water, ethylacetate and water. The ether was distilled over sodium, the ethylacetate dried with calcium chloride and fractionated, the boiling point rising a full degree for a liter distilled off. I think, however, that no essential error was introduced in this way, and that, for my purposes, it was sufficiently pure. The solubilities were determined volumetrically. In all cases I took 10 c.c. of the solvent in a test tube and ran in the solute from a burette till the solution clouded. One can determine this point to 0.01 c.c without difficulty. In Table VIII. I give the solubilities at 20° expressed in cubic centimeters of solute in 10 c.c. of solvent. The solubilities of ether and ethylacetate

in water decrease with increasing temperature; the solubilities of water in ether and ethylacetate increase with increasing temperature. This behavior is well known for ether; but I have not found it stated anywhere for ethylacetate.

TABLE VIII.

Solute.	Solvent.	Solubility.
Ether	Water	1.03–4[1]
Water	Ether	0.08
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294

It will be remembered that, when two liquids were practically non-miscible, the series of saturated solutions formed by these with a consolute liquid were expressed by two curves of the same general form, but having different constants; and it was found that these two curves represented, the one the series of solutions out of which liquid *B* is precipitated on addition of either *A* or *B*; the other, the converse series, when the solution was saturated in respect to *A* but sensitive to an excess of either *A* or *B*. When the liquids *A* and *B* are partially miscible, the case becomes apparently more complicated, for we have four curves instead of two. These refer to four distinct sets of equilibrium, there being the following four series of saturated solutions.

1. The solution is saturated in respect to *B*. Excess of *A* produces no precipitate.

2. The solution is saturated in respect to *B*. Excess of *A* or *B* produces a precipitate of *B*.

3. The solution is saturated in respect to *A*. Excess of *A* or *B* produces a precipitate of *A*.

4. The solution is saturated in respect to *A*. Excess of *B* produces no precipitate.

Series 2 and 3 correspond to the two series observed with two non-miscible liquids. In these two series the consolute liquid is the solvent, whereas in series 1 and 4 we have, in addition, *A* and

[1] Schuncke finds 1.04–5, Zeitschr. f. ph. Chem., XIV. 334. 1894.

B respectively as solvents. In Tables IX.–XIII. I give the measurements made with ether and water, ethylacetate and water with the consolute liquids alcohol, methylalcohol, and acetone. In Tables IX. and XI. the experiments were made with saturated solutions; in Tables X., XII., and XIII., with pure liquids. The first method has the advantage that the readings obtained are final, involving no correction and no knowledge of the mutual solubilities. On the other hand, it is necessary to keep the solutions in the burettes at the same temperature as that at which one makes the determinations, a very difficult thing to do usually, so that the second method is to be preferred. The exponential factors are the same according to both methods, as I have already shown. The integration constants are different, standing to each other in the relation given in Equation (18). It would have been well if I had determined the densities of the saturated solutions so that they could be recalculated into cubic centimeters of the pure liquids; but I shall have to make an extended series of density determinations in connection with the equilibrium between two liquid phases, and I have postponed these others till then. The measurements in Tables IX.–XIII. are about as accurate as those in Tables I.–VI., with the exception of the solutions when water is part solvent. The precipitate in these cases is lighter than the solution, consists of a few drops only, and is very difficult to distinguish from air bubbles, especially in the ether solutions, where the clouding at best is very slight. For this reason the first series in each table must be considered as very doubtful as the absolute measurements go. The determination of the saturation point for these cases depended on the light, the state of my eyes, and the mood which I happened to be in on the days when the measurements were made. So difficult are the determinations sometimes, that I give no results for ether-water-acetone because I obtained different measurements every day. The agreement between the observed and the theoretical values is no test of the absolute accuracy of either; but merely shows that the solutions follow the same general law, the constants, exponential, and integration, varying with the degree of cloudiness which the observer takes as denoting the point of saturation. The values of n are not so accu-

rate as in the first set of tables, because the curves cover a more limited extent, and therefore the variations are smaller, and because when the value of n is large, say over 2, a very slight change in the direction of the logarithmic curve produces a very large corresponding change in n. The amounts of ethylacetate and water which dissolve in 5 c.c. of alcohol, methylalcohol, or acetone were so large that I was forced to work with one cubic centimeter of these liquids as solvent.

TABLE IX.

X c.c. Sat. Water; Y c.c. Sat. Ether; 5 c.c. Alcohol. Temp. 20°.

Formula $XY^{n_1} = C_1$; $n_1 = 2.60$; $\log C_1 = 1.994$.

Sat. Water.		Sat. Ether.		$\log C_1$.
Calc.	Found.	Calc.	Found.	
49.89	50.00	1.30	1.30	1.995
24.89	25.00	1.70	1.70	1.996
10.02	10.00	2.41	2.41	1.993
Average,				1.995

Formula $X^{n_2}Y = C_2$; $n_2 = 1.49$; $\log C_2 = 1.867$.

				$\log C_2$.
9.04	9.00	2.79	2.77	1.864
7.96	8.00	3.33	3.35	1.870
7.72	7.70	3.52	3.50	1.865
6.00	6.00	5.10	5.10	1.867
Average,				1.867

Formula $XY = C_3$; $\log C_3 = 1.493$.

				$\log C_3$.
5.19	5.21	5.97	6.00	1.495
4.45	4.45	7.00	7.00	1.493
3.99	4.00	7.78	7.80	1.494
3.89	3.87	8.03	8.00	1.491
3.11	3.10	10.05	10.00	1.491
2.08	2.08	14.95	15.00	1.495
1.78	1.77	17.58	17.50	1.491
Average,				1.493

TABLE IX. (*continued*).

Formula $X^{n_4}Y = C_4$; $n_4 = 1.73$; $\log C_4 = 1.665$.

Sat. Water.		Sat. Ether.		$\log C_4$.
Calc.	Found.	Calc.	Found.	
1.62	1.61	20.28	20.00	1.661
1.43	1.43	24.95	25.00	1.673
1.09	1.10	39.27	40.00	1.666
0.96	0.95	50.47	50.00	1.659
Average, ...				1.665

TABLE X.

x c.c. Water; y c.c. Ether; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.008\,y)(y - 0.103\,x)^{n_1} = C_1$; $n_1 = 1.50$; $\log C_1 = \bar{1}.502$

Water.		Ether.		$\log C_1$.
Calc.	Found.	Calc.	Found.	
10.05	10.00	1.13	1.13	$\bar{1}$.500
9.00	9.00	1.04	1.04	$\bar{1}$.502
7.03	7.00	0.85	0.85	$\bar{1}$.500
4.97	5.00	0.68	0.68	$\bar{1}$.505
4.00	4.00	0.60	0.60	$\bar{1}$.502
				$\bar{1}$.502

Formula $(x - 0.008\,y)^{n_2}(y - 0.103\,x) = C_2$; $n_2 = 1.13$; $\log C_2 = \bar{1}.928$.

				$\log C_2$.
2.95	3.00	0.555	0.56	$\bar{1}$.936
2.50	2.50	0.56	0.56	$\bar{1}$.928
2.03	2.00	0.60	0.59	$\bar{1}$.920
1.80	1.80	0.63	0.63	$\bar{1}$.929
1.50	1.50	0.70	0.70	$\bar{1}$.929
				$\bar{1}$.928

TABLE X. (*continued*).

Formula $(x - 0.008y)^{n_3}(y - 0.103x) = C_3$; $n_3 = 2.04$; log $C_3 = 0.045$.

Water.		Ether.		log C_3.
Calc.	Found.	Calc.	Found.	
1.20	1.20	0.90	0.90	0.047
1.00	1.00	1.23	1.23	0.045
0.90	0.89	1.53	1.50	0.035
0.83	0.83	1.79	1.80	0.047
0.78	0.78	2.00	2.00	0.046
0.64	0.64	3.01	3.00	0.043
0.57	0.57	3.99	4.00	0.047
0.52	0.52	5.00	5.00	0.045
0.47	0.47	6.89	7.00	0.053
				0.045

Formula $(x - 0.008y)^{n_4}(y - 0.103x) = C_4$; $n_4 = 4.4$; log $C_4 = \bar{1}.057$.

				log C_4.
0.44	0.44	10.30	10.00	$\bar{1}$.044
0.45	0.45	11.62	12.00	$\bar{1}$.071
0.45	0.45	15.04	15.00	$\bar{1}$.056
				$\bar{1}$.057

TABLE XI.

X c.c. Sat. Water; *Y* c.c. Sat. Ethylacetate; 1 c.c. Alcohol. Temp. 20°.

Formula $XY^{n_1} = C_1$; $n_1 = 2.86$; log $C_1 = \bar{1}.280$.

Sat. Water.		Sat. Ethylacetate.		log C_1.
Calc.	Found.	Calc.	Found.	
10.05	10.00	0.25	0.25	$\bar{1}$.278
8.07	8.00	0.27	0.27	$\bar{1}$.276
7.11	7.00	0.28	0.28	$\bar{1}$.263
5.97	6.00	0.30	0.30	$\bar{1}$.282
4.97	5.00	0.32	0.32	$\bar{1}$.283
3.94	4.00	0.34	0.35 –	$\bar{1}$.286
Average, ...				$\bar{1}$.278

TABLE XI. (*continued*).

Formula $X^{n_2}Y = C_2$; $n_2 = 1.80$; $\log C_2 = 0.549$.

Sat. Water.		Sat. Ethylacetate.		$\log C_2$.
Calc.	Found.	Calc.	Found.	
3.00	3.00	0.49	0.49	0.549
2.50	2.50	0.68	0.68	0.548
2.00	2.00	1.02	1.02	0.550
Average, ...				0.549

Formula $X^{n_3}Y = C_3$; $n_3 = 1.36$; $\log C_3 = 0.433$.

				$\log C_3$.
1.45	1.50	1.56	1.59	0.445
1.25	1.25	2.00	2.00	0.433
1.06	1.06	2.51	2.50	0.432
1.00	1.00	2.71	2.72	0.434
0.93	0.92	3.04	3.00	0.428
0.75	0.75	4.00	4.00	0.432
Average, ...				0.434

Formula $X^{n_4}Y = C_4$; $n_4 = 1.765$; $\log C_4 = 0.372$.

				$\log C_4$.
0.65	0.65	5.02	5.00	0.369
0.59	0.59	5.98	6.00	0.373
0.54	0.54	7.00	7.00	0.372
0.50	0.50	8.00	8.00	0.372
0.44	0.44	9.96	10.00	0.370
Average, ...				0.371

TABLE XII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.029y)(y - 0.093x)^{n_1} = C_1$; $n_1 = 1.20$; $\log C_1 = 0.002$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
9.92	10.00	1.08	1.08	0.006
6.96	7.00	0.85	0.85	0.005
5.08	5.00	0.72	0.72	$\bar{1}$.995
3.96	4.00	0.69	0.69	0.006
3.01	3.00	0.68	0.68	0.000
2.51	2.50	0.70	0.70	0.001
Average,				0.002

Formula $(x - 0.029y)^{n_2}(y - 0.093x) = C_2$; $n_2 = 2.78$; $\log C_2 = 0.631$.

				log C_2.
2.03	2.00	0.83	0.82	0.637
1.80	1.80	1.04	1.04	0.630
1.72	1.70	1.19	1.15	0.617
1.49	1.50	1.63	1.69	0.644
1.41	1.41	1.99	2.00	0.633
Average,				0.632

Formula $(x - 0.029y)^{n_3}(y - 0.093x) = C_3$; $n_3 = 2.00$; $\log C_3 = 0.550$.

				log C_3.
1.29	1.29	2.51	2.50	0.549
1.20	1.20	2.99	3.00	0.551
1.07	1.07	4.03	4.00	0.547
1.00	1.00	4.88	4.90	0.552
Average,				0.550

Formula $(x - 0.029y)^{n_4}(y - 0.093x) = C_4$; $n_4 = 7.00$; $\log C_4 = 0.078$.

				log C_4.
0.97	0.97	6.00	6.00	0.078
0.98	0.98	7.02	7.00	0.076
1.00	1.00	7.61	8.00	0.100
1.03	1.03	9.98	10.00	0.079
Average,				0.083

Table XIII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Acetone. Temp. 20°.

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_1} = C_1$; $n_1 = 1.54$; $\log C_1 = \bar{1}.364$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	$\log C_1$.
10.12	10.00	1.02	1.01	$\bar{1}.359$
6.99	7.00	0.76	0.76	$\bar{1}.365$
5.01	5.00	0.60	0.60	$\bar{1}.363$
3.00	3.00	0.47	0.47	$\bar{1}.364$
2.00	2.00	0.43	0.43	$\bar{1}.365$
Average,				$\bar{1}.363$

Formula $(x - 0.029\,y)^{n_2}\,(y - 0.093\,x) = C_2$; $n_2 = 1.16$; $\log C_2 = \bar{1}.721$.

				$\log C_2$.
1.50	1.50	0.47	0.47	$\bar{1}.721$
1.00	1.00	0.63	0.63	$\bar{1}.721$
Average,				$\bar{1}.721$

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_3} = C_3$; $n_3 = 1.26$; $\log C_3 = \bar{1}.653$.

				$\log C_3$.
0.79	0.80	0.74	0.74	$\bar{1}.656$
0.69	0.69	0.80	0.80	$\bar{1}.652$
0.51	0.51	1.00	1.00	$\bar{1}.652$
0.31	0.31	1.50	1.50	$\bar{1}.653$
Average,				$\bar{1}.653$

Formula $(x - 0.029\,y)^{n_4}\,(y - 0.093\,x) = C_4$; $n_4 = 3.00$; $\log C_4 = \bar{2}.135$.

				$\log C_4$.
0.25	0.25	2.01	2.00	$\bar{2}.134$
0.25 –	0.25	2.48	2.50	$\bar{2}.138$
0.286	0.285	3.01	3.00	$\bar{2}.134$
0.29	0.29	5.00	5.00	$\bar{2}.135$
Average,				$\bar{2}.135$

In this set of tables, as in the first set, the amount of one non-miscible liquid which will dissolve in the consolute liquid decreases

as the quantity of the other non-miscible liquid increases. In this case, however, the non-miscible liquids are saturated solutions, and it does not follow that the quantity of one pure liquid decreases as the other increases. There comes a point where the rate of increase of one component in the solution in which it is solute is greater than its rate of decrease in the solution in which it is solvent. If we take the general equation (17),

$$(x-s_2y)^n(y-s_1x)=C_2,$$

it is obvious that as x increases y will first decrease, pass through a minimum, and then increase. If the same equation expressed the two equilibria, the point where y was a minimum would be the point where the solution is no longer sensitive to an excess of x. In general, the equilibrium for this second stage is given by a second equation, and all we can say in our present knowledge is that at the intersection of these two curves y should have a minimum value. This does not seem to hold in Table XII., where the amount of ethylacetate soluble in 1 c.c. methylalcohol in presence of 2.50 c.c. water is more than will dissolve when either three or four cubic centimeters of water are added. I am inclined to attribute this to experimental error, as I do not see how there can be two saturated solutions of the same substance in the same solvent. Such a case would be entirely new, and would involve such consequences that it is not to be assumed on the strength of a variation of two one-hundredths of a cubic centimeter in measurements where the probable error is known to be very large. I propose to repeat these measurements on a larger scale, so as to determine what the facts really are. There are also one or two things in respect to the ether-water-methylalcohol curve which need to be gone into more closely. In Table XIV. I give the values for log C when cleared of the term for z, and the values for log K when the effect of the exponential factor has been eliminated. Both log C and log K are calculated for x, y, and z, being expressed in cubic centimeters. A discussion of these values is not possible at present, and in any case they should be reduced to reacting volumes or reacting weights before a rational treatment could be thought of.

TABLE XIV.

Mixtures.	log C_1.	log C_2.	log C_3.	log C_4.	log K_1.	log K_2.	log K_3.	log K_4.
S. H_2O, S. Ether, Alcohol	Ī.478	0.126	0.095	Ī.757	Ī.855	0.051	0.047	Ī.911
H_2O, Ether, Methylalcohol	Ī.502	Ī.928	0.045	Ī.057	Ī.801	Ī.966	0.015	Ī.825
S. H_2O, S. Et. Ac., Alcohol	Ī.280	0.549	0.433	0.372	Ī.814	0.196	0.182	0.134
H_2O, Et. Ac., CH_3OH	0.002	0.631	0.550	0.078	0.001	0.167	0.183	0.001
H_2O, Et. Ac., Acetone	Ī.364	Ī.721	Ī.653	2.135	Ī.749	Ī.871	Ī.894	Ī.534

The measurements already communicated would be sufficient by themselves to establish the general law governing this class of equilibria; but I have in addition experiments by other investigators which give the same result. In 1871 Tuchschmidt and Follenius[1] noticed that carbon bisulphide was not infinitely miscible with aqueous alcohol, and they made a series of experiments to determine the saturation points when carbon bisulphide was added to alcohol of known strengths. They expressed their results by means of a complex empirical formula. This is not necessary, as the general equation for two non-miscible liquids cover the case entirely. In Table XV. the first column gives the number of cubic centimeters of carbon bisulphide which will dissolve in ten cubic centimeters of aqueous alcohol of the percentage composition by weight given in column two. In column three is the strength of alcohol as required by the formula.

TABLE XV.

x = g. H_2O; y = c.c. CS_2. Temp. 17°.

Formula $xy^n = C$; $n = \frac{5}{3}$; log $C = 1.345$.

Per cent Alcohol.			
y.	Calc.	Found.	log C.
18.20	98.8	98.5	1.457
13.20	98.0	98.15	1.318
10.00	97.0	96.95	1.345
7.00	95.0	93.54	1.456
5.00	91.5	91.37	1.350
3.00	84.3	84.12	1.324
2.00	74.0	76.02	1.310
0.20	—	48.4	—
Average, ...			1.366

[1] B. B., IV. 583. 1871.

When one considers that the carbon bisulphide was evidently determined very roughly, the agreement is an excellent one. Here, too, we find the existence of two curves. The last measurement lies on the second curve when water is the precipitate, and not carbon bisulphide. As only one point on this curve was measured, it is impossible to determine the constants even approximately. The object of this investigation by Tuchschmidt and Follenius was to obtain a method for determining the strength of aqueous alcohol quickly and easily. Owing to the unpleasant properties of carbon bisulphide, their choice of liquids was bad, though the method seems to me a good one. If one were to make a complete table for benzol or chloroform and aqueous alcohol at zero degrees, the rest would be simplicity itself. One would take ten cubic centimeters of the alcohol to be tested and run in chloroform from a burette till saturated, when a glance at the table would give the percentage composition of the alcohol. The method would be quicker than any except with a hydrometer, and more accurate than that. An idea of the accuracy is given by the fact that at 20°, 5 c.c. of 96 per cent alcohol require about 20 c.c. chloroform, while the same amount of 97.5 per cent alcohol requires about 30 c.c. for saturation. For a weaker alcohol the change for each per cent is much less; but the measurements can be made more accurately.

I will now take up the measurements of Pfeiffer[1] on the miscibility of various esters with alcohol and water. The measurements were not made under the most favorable circumstances. A known amount of the ester was poured into a beaker, a definite quantity of alcohol added, and water run in till the saturation point was reached. Nothing was done to prevent evaporation, nothing, so far as is mentioned, to keep a constant temperature, and there was no means of warming the solution above the final temperature in order to insure that equilibrium had been reached. The necessity of this last had already been pointed out by Duclaux,[2] who found that, on cooling a solution below its saturation point, it clouded at once; but on warming, the equilibrium was

[1] Zeitschr. f. ph. Chem., IX. 469. 1892.
[2] Ann. chim. phys., [5.], VII. 264. 1876.

reached much more slowly. Given these untoward conditions, the comparative accuracy of the measurements is remarkable. While Pfeiffer has given us series upon series of valuable measurements, showing the increase of miscibility of esters and water in presence of alcohol, he has curiously enough omitted all determinations of the miscibility of water and esters when no alcohol is present. This is still more remarkable if one considers the uselessness of comparing the effect of equal quantities of alcohol on ethylacetate and water, amylacetate and water, without allowing for the fact that ethylacetate is roughly forty times as soluble in water as amylacetate. As these solubilities had to be known at any rate approximately, in order to apply Equation II. to Pfeiffer's experimental data, I have determined several myself. Through the courtesy of Mr. Dunlap of the organic laboratory, I received small quantities of ethylbutyrate, ethylisovalerate, and isoamylacetate. I dried them over calcium chloride and fractionated. The change of boiling point of the portions used was four degrees for the ethylisovalerate and two degrees for each of the others. The amounts at my disposal made it not worth while to attempt further purification. In Table XVI. I give the solubilities in cubic centimeters of the solute in ten cubic centimeters of the solvent at 20°. For purposes of comparison I have also inserted in this table the values for ethylacetate from Table VIII.

TABLE XVI.

Solute.	Solvent.	Solubility.
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294
Isoamylacetate	Water	0.02
Water	Isoamylacetate	0.12
Ethylbutyrate	Water	0.08
Water	Ethylbutyrate	0.04–5
Ethylisovalerate	Water	0.02–
Water	Ethylisovalerate	0.04+

For these four esters I have found that the solubility in water decreases with increasing temperature, while the solubility of

water in the ester increases with increasing temperature, both observations being made at 20°. As there is no obvious reason why these four esters should all be abnormal, it is more than likely that this behavior is characteristic of all esters at ordinary temperatures. As it is improbable that the solubility of the esters in water can continue to decrease indefinitely with increasing temperature, there must be some point where it reaches a minimum, and it is quite possible that a determination of this temperature for different esters might give interesting results. The experiments could be made with great ease, as the amount of saponification during the time necessary for a measurement would be very small.

Quite recently, de Hemptinne[1] has determined the solubilities of several esters in water at 25°. His measurements are given in grams of the solute per liter of solution. I have reduced his measurements to cubic centimeters of solute in ten cubic centimeters of solvent by dividing by the densities as far as I could get them out of Landolt and Börnstein's tables and Roscoe and Schorlemmer's text-book, disregarding the difference between a liter of solution and a liter of solvent. The results which I give in Table XVII. are only rough approximations, but quite sufficient for my purpose. The figures in the second column are the densities used in recalculating de Hemptinne's figures.

TABLE XVII.

Solute.	Solubility.	Density.
Isobutylacetate	0.07	0.88
Amylacetate	0.02−	0.88
Methylbutyrate	0.115	0.94
Ethylbutyrate	0.08−	0.898
Amylbutyrate	0.006	0.85
Propylpropionate	0.06+	0.88
Amylpropionate	0.01+	0.88
Ethylvalerate	0.03	0.86

De Hemptinne did not measure the solubility of water in the esters, and I have not been able to find any data on the subject

[1] Zeitschr. f. ph. Chem., XIII. 561. 1894.

beyond the few measurements which I have made myself. In considering Pfeiffer's results, this is not very serious, because he worked always with three cubic centimeters of esters, adding alcohol in varying quantities, and water to saturation. As the solubility of water in the different esters can be rarely more than one per cent, the error in calculating the amount of water required to saturate will in no case be more than a tenth of a cubic centimeter, and will rarely exceed two or three hundredths. The solubilities of esters in water, which have not been determined by de Hemptinne or myself, have been filled in as best I could by analogy, remembering that increase of carbon means decrease of solubility, and that among isomeric esters the one with the smaller acid radical was rather the less soluble. In deciding where between two limits an unknown solubility should be put, I have taken the figure which satisfied the experimental data best. The solubilities thus obtained lay no claim to being accurate; but they are not very far out, probably in no case more than 100 per cent, and this rough approximation is better than treating the esters and water as absolutely non-miscible. In Table XVIII. I give the solubilities which I have used in calculating Pfeiffer's results, expressed in cubic centimeters of the ester in ten cubic centimeters of water.

TABLE XVIII.

Solute.	Solubility.	Solute.	Solubility.
Methylvalerate	0.20	Propylacetate	0.30
Ethylvalerate	0.03	Butylacetate	0.07
Methylbutyrate	0.12	Amylacetate	0.02
Ethylbutyrate	0.08	Propylformiate	0.40
Propylbutyrate	0.02	Butylformiate	0.10
Ethylpropionate	0.30	Amylformiate	0.05
Propylpropionate	0.065		

Starting, as Pfeiffer did, with a constant quantity of ester, his results necessarily lie almost entirely along the curve representing the equilibrium when addition of water or ester produces a pre-

cipitate of ester. In a few cases there are a few measurements, never more than two, on the curve where water or ester produces a precipitate of water. There are not enough of these measurements to enable me to determine the direction of this second curve, and in the tables I have therefore given no calculated values in these cases. The point where, according to Pfeiffer, infinite miscibility occurs is the beginning of the curve where the solution is saturated in regard to ester; but water produces no precipitate. The corresponding curve where the solution is saturated in respect to water, while addition of ester produces no precipitate, did not come within the scope of Pfeiffer's investigations at all. It will be noticed that in the last measurements of each series the amount of water required to saturate is very generally greater than the theoretical quantity. I attribute this variation entirely to experimental error. When one is working with one hundred cubic centimeters of solution or more, it becomes almost impossible to determine the first appearance of clouding with great accuracy. In Tables XIX. to XXXI. I give Pfeiffer's results, with the values for the water calculated according to the formula at the top of each table. It is only fair to Herr Pfeiffer to say that, if I had arranged the exponential factors so that z should have been raised to the first power only, the differences between the observed and the calculated values would have been less than they now are. I felt, however, that, as the water was the thing I was calculating, I would make its exponential factor unity instead of that of the alcohol.

[*To be continued.*]

TABLE XIX.

$y = 3$ c.c. Methylvalerate; x = c.c. Water; z = c.c. Alcohol.

Formula $x(y - 0.02\,x)^{0.37}/z^{1.37} = C$; log $C = \bar{1}.807$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.66	—
6	5.04	5.06	$\bar{1}.809$
9	8.88	9.03	$\bar{1}.815$
12	13.28	13.40	$\bar{1}.809$
15	18.34	18.41	$\bar{1}.809$
18	23.90	24.00	$\bar{1}.809$
21	30.09	30.09	$\bar{1}.807$
24	36.80	36.72	$\bar{1}.806$
27	44.35	44.15	$\bar{1}.805$
30	52.80	52.37	$\bar{1}.803$
33	62.60	62.25	$\bar{1}.804$
36	74.25	74.15	$\bar{1}.806$
39	91.45	91.45	$\bar{1}.807$
42	—	∞	$\bar{1}.807$

TABLE XX.

$y = 3$ c.c. Ethylvalerate; x = c.c. Water; z = c.c. Alcohol.

Formula $x\,(y - 0.003)^{0.40}/z^{1.40} = C$; log $C = \bar{1}.682$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.42	—
6	3.81	4.14	$\bar{1}.718$
9	6.73	7.18	$\bar{1}.710$
12	10.07	10.51	$\bar{1}.701$
15	13.81	14.13	$\bar{1}.692$
18	17.80	18.09	$\bar{1}.688$
21	22.15	22.40	$\bar{1}.687$
24	26.80	26.83	$\bar{1}.683$
27	31.65	31.70	$\bar{1}.683$
30	36.70	36.62	$\bar{1}.681$
33	42.15	41.81	$\bar{1}.678$

TABLE XX (*continued*).

z.	Calc.	Found.	log *C*.
36	47.65	48.00	$\bar{1}$.685
39	53.40	53.13	$\bar{1}$.679
42	59.40	58.35	$\bar{1}$.674
45	65.55	63.60	$\bar{1}$.668
48	71.90	69.97	$\bar{1}$.670
51	78.50	76.90	$\bar{1}$.672
54	83.25	84.25	$\bar{1}$.688
57	92.40	90.53	$\bar{1}$.673
60	99.50	98.60	$\bar{1}$.678
63	106.80	105.20	$\bar{1}$.675
66	114.70	112.80	$\bar{1}$.674
69	122.40	121.90	$\bar{1}$.680
72	130.40	131.00	$\bar{1}$.684
75	138.90	140.20	$\bar{1}$.687
78	148.00	158.70	$\bar{1}$.712
81	157.50	180.00	$\bar{1}$.740
			$\bar{1}$.687

TABLE XXI.

$y = 3$ c.c. Methylbutyrate; x = c.c. Water; z = c.c. Alcohol.

Formula $x\,(y - 0.012)^{0.52}/z^{1.52} = C$; log $C = \bar{1}.888$.

	x.		
z.	Calc.	Found.	log *C*.
3	2.33	2.34	$\bar{1}$.889
6	6.75	6.96	$\bar{1}$.902
9	12.67	12.62	$\bar{1}$.886
12	19.90	19.45	$\bar{1}$.878
15	28.38	28.13	$\bar{1}$.884
18	38.76	38.80	$\bar{1}$.889
21	50.85	55.64	$\bar{1}$.927
24	—	∞	$\bar{1}$.892

MINOR CONTRIBUTIONS.

On a Simple Method of Photographically Registering the Infra-Red Energy Spectrum.[1]

By Knut Ångström.

UP to the present time it has been possible to photograph directly only an extremely small part of the infra-red spectrum, and the spectro-bolometric method is still the only one which affords us a means of obtaining a more intimate knowledge of the distribution and intensity of the longer wave-lengths. It is also to be noted that this method gives a means of comparing the different parts of the spectrum *quantitatively*, which is scarcely possible by photography. The investigation of the infra-red spectrum with the aid of the spectro-bolometer is nevertheless so tedious, and, with the apparatus which has heretofore been commonly used, occupies so much time, that we might safely predict that unless the method is further developed, it will be possible to continue investigation in this field only very slowly.

In a communication to the British Association on August 11, 1894, Professor Langley, who was the first to develop the spectro-bolometric method, has so perfected this method that the work can now be carried out in the infra-red almost as easily, and with almost as great accuracy, as in other regions of the spectrum. This is made possible partly by such refinement in the construction of the optical parts of the instrument as has heretofore never been reached; partly, also, by substituting for the observer a photographic plate. As the result of the optical improvements, such sharpness and dispersive powers were gained that the instrument not only shows both of the *D* lines, but also the nickel line in the solar spectrum lying between the two. Through the possibility of recording the indications of the spectro-bolometer by photographic methods the labor of the observer is of course lightened in the highest degree.

The principle of the new method is briefly the following: —

The telescope and scale of the galvanometer are replaced by the photographic plate, upon which falls a beam of light reflected from the mirror of the galvanometer. The telescope of the spectro-bolometer is driven by

[1] A paper presented to the Royal Society of Sciences of Upsala, April 10, 1895.

accurate clock-work, which also gives to the photographic plate a vertical movement. The motor is constructed with such accuracy that the two movements, viz. that of the telescope and that of the plate, are as nearly as possible synchronous. For each minute of arc through which the bolometer wire is moved, the photographic plate moves one centimeter.

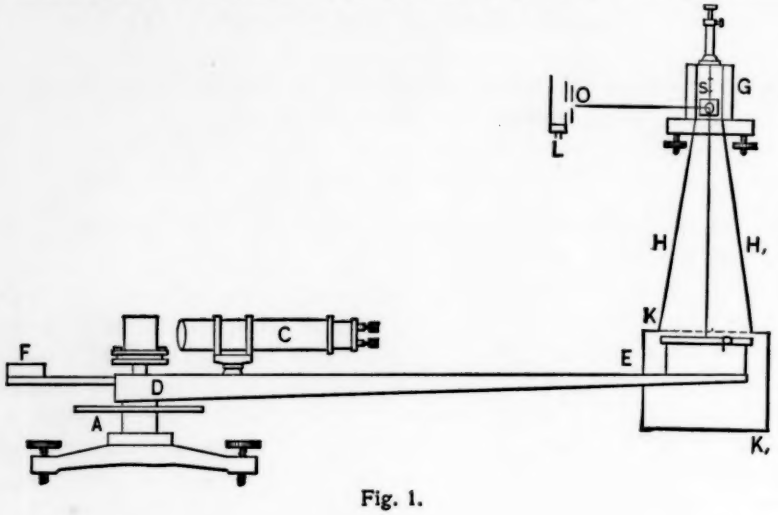

Fig. 1.

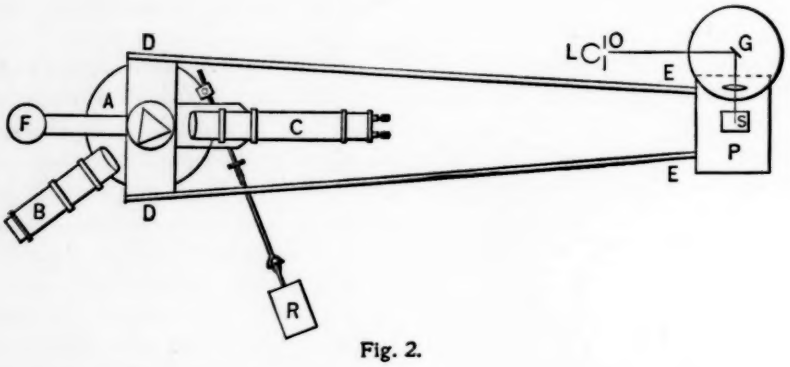

Fig. 2.

With the instrument constructed by Langley it appears that the extreme limits of sensitiveness and sharpness which are possible with the methods and apparatus at our disposal, have been reached. Such an instrument, however, can only be obtained by a richly endowed laboratory. For that reason I have undertaken the problem of simplifying the photographic method of registration, and shall describe below an apparatus which seems to offer a satisfactory solution.

The essential difference between this instrument and that of Langley consists in the fact that the photographic plate is rigidly fastened to the bolometer tube, so that both can be moved at the same time. The beam of light reflected from the mirror of the galvanometer is then thrown upon the moving plate. The movement of the spot of light resulting from a rotation of the galvanometer mirror, must, however, take place in a direction at right angles to the motion of the plate. In order to accomplish this, the apparatus is arranged as shown in Figs. 1 and 2.

The light horizontal arm DE is fastened to the rather solidly built support A of the telescope, so that the former may be rotated with the tube C of the bolometer. The photographic plate with its holder is placed in a horizontal position at the end of this arm. Almost vertically above the plate stands the galvanometer G which is used with the bolometer. The light from the source L passes through a slit O and falls upon the mirror of the galvanometer at an angle of 45 degrees. After reflection the beam is brought into a vertical direction by means of the mirror S, and the image of the slit falls upon the photographic plate P. When the galvanometer mirror is rotated, this image moves in the direction of the bolometer arm (in the plane of the drawing in Fig. 2). If the arm is rotated, however, the beam of light describes a line perpendicular to the first direction. If the tube, and with it the arm DE, is rotated, the bolometer wire passes through the different portions of the spectrum, and the galvanometer gives for each position the corresponding intensity of the radiation. The position of the spot of light upon the plate is thus determined at each instant by the position of the arm and the position of the galvanometer mirror. In the curve which the spot of light describes under these circumstances, distances perpendicular to the arm are therefore proportional to the angular position in the spectrum, while distances in the direction of the arm are proportional to the intensity corresponding to this position. Since the photographic plate and the bolometer wire are rigidly connected, the movements are here of necessity absolutely synchronous.

Between the galvanometer mirror and the mirror S a lens is placed which throws a sharp image of the slit O upon the plate. The latter is surrounded by a small box KK_1 in order to cut out stray light, and for the same reason a conical pasteboard tube HH_1 is placed upon the box. One side of the box is formed of two parts, which can be taken off in order to make it easier to remove the plate. Between them is a horizontal opening four centimeters wide to allow a free movement of the arm. The upper cover has a very narrow slit extending in the direction of the bolometer arm, by means of which the image (whose length is perpendicular to the opening of this slit) is limited practically to a point.

With this arrangement, a means of moving the telescope with extreme

accuracy is entirely unnecessary. The only requirement is that the movement of the bolometer tube should take place rather uniformly, and without jerks. I have used with good results a very simple clock-work for this purpose, the movement being damped by an air cushion. By varying the adjustment of the latter the rapidity of the motion could be regulated. The most rapid rotation which I have used was ten minutes of arc per minute. In this case the length of the arm, and therefore the distance from the axis of the spectrometer, was two meters. A rotation of the bolometer tube through an angle of one degree thus caused the image to describe an arc on the photographic plate 3.48 cm. long; or, in other words, each minute of arc corresponded to the movement of the plate of 0.58 mm. If it is desired to have the movement of the plate greater, this can of course be accomplished by lengthening the arm. In connection with the apparatus at my disposal the motion of the plate mentioned above was, however, sufficiently great. For the preliminary investigation of many questions, also, a greater dispersion of the spectrum is hardly necessary.

I shall take this occasion to mention also another solution of the problem of photographically registering the indications of a bolometer, although I have not yet tested the method. Figure 3 indicates the arrangement. The ray of light proceeds from the galvanometer mirror G to the mirror S, making an angle of 45° with the latter. It is here reflected in a vertical direction, and then by means of mirror S_2, whose plane is perpendicular to the plane of the first mirror S_1, again reflected in a horizontal direction and projected upon the photographic plate. The last mirror is fastened upon the bolometer tube T above the axis of the spectrometer. On rotating the tube, the spot of light moves upon the plate in a horizontal direction, while if the galvanometer mirror rotates, the motion of the spot of light is in a vertical direction. This arrangement has the advantage that the movement can more easily be made much greater. For example, if the distance between S_2 and P is five meters, the spot of light will move 2.9 mm. in a horizontal direction for a rotation of the theodolite of one minute.

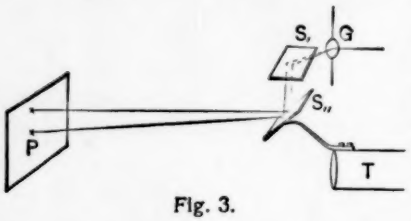

Fig. 3.

Up to the present time I have had an opportunity of testing the first method only in the case of the radiation from gas flames. I have, however, been able to convince myself of the practicability of the method. In addition to the two large maxima first discovered by Julius, and whose origin was more carefully investigated by myself, the photographic record of the spectrum of the Bunsen flame shows very clearly the two small

maxima lying nearer to the visible portion of the spectrum. The latter maxima have been given by Paschen in the radiation of the oxyhydrogen flame and the Bunsen flame. For the case of a rock salt prism with a refracting angle of 60°, the positions of these four maxima as indicated by their angular deviation from the *D* line are as follows: —

1° 25′ 12″ corresponding to $\lambda = 1.48\,\mu$;
1° 34′ 32″ corresponding to $\lambda = 1.96\,\mu$;
1° 45′ 35″ corresponding to $\lambda = 2.80\,\mu$;
2° 6′ 0″ corresponding to $\lambda = 4.34\,\mu$.

In this brief preliminary note I have merely wished to show the possibility of obtaining a photographic registration of bolometer indications with comparatively simple apparatus; and that it is possible to construct an instrument which shall at least bear the same relation to that of Langley as does the direct-vision spectroscope to the larger instruments of its class.

On the Electrolytic Conductivity of Concentrated Sulphuric Acid.

By Dr. K. E. Guthe and L. J. Briggs.

It is a well-known fact that the specific conductivity as well as the molecular conductivity of sulphuric acid is a minimum for a concentration corresponding closely to the hydrate $H_2SO_4 + H_2O$. The investigations of F. Kohlrausch, Bouty, and Ostwald have shown, moreover, that this minimum becomes less pronounced, the higher the temperature is. Seemingly this acid forms an exception to the rule that the water of crystallization has no influence upon the conductivity of electrolytes. Our experiments were undertaken in order to provide more data for solutions of this acid at a concentration near 84.5 per cent (corresponding to the hydrate), with reference to the changes produced by temperature.

Similar work has been done by Miss Klaassen[1], but since her work may include errors of even more than 2 per cent we have repeated part of it. The conclusions drawn from our experiments are new.

Experiments as to the conductivity of the hydrate in the solid state have to our knowledge not been published before.

Our arrangement differs in some points from the usual one. As the source of electricity we used an alternating current, produced by a two-phase dynamo designed by Professor Carhart and represented in the accompanying cut. The field is formed by a revolving electromagnet excited by

[1] Proc. of Cambr. Phil. Soc., Vol. VII., p. 137.

an independent current from the storage battery which can be varied at will. In our experiments we used, of course, the sinusoidal current from only one pair of terminals. The bridge was formed by an ordinary slide wire bridge of manganin wire, lengthened by additional strictly non-inductive resistances of the same metal (each of 26 ohms' resistance = 6360 cm. of the bridge). Instead of a telephone we took a very sensitive electrodynamometer, the stationary coils of which were connected in parallel with the bridge.

Since we used for the determination of temperature a calibrated ordinary thermometer, which could not be read more accurately than to one-twentieth

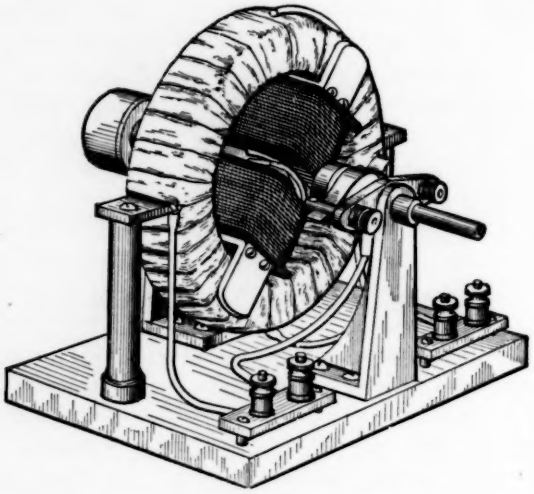

Fig. 1.

of a degree, we arranged the conditions so that the errors of observation would not exceed 0.1 per cent. For this purpose we sent only 0.8 ampere through the field of the generator. Since this current can easily be increased to 16 or more amperes, one can apply this arrangement for the measurement of conductivity of bad conductors just as well. The objection to the use of alternating currents for such a purpose raised by M. Wildermann [1] cannot be applied here. The time spent for one observation is very short, and not longer than that necessary for the determination by telephone.

The specific gravity in each case was determined by a delicate Mohr's balance, and from this value the concentration obtained. All calculations necessary were based upon the data given in Landolt and Boernstein's Tabellen (2d ed.).

[1] Zeitschr. f. phys. Chemie, 14, p. 247, 1894.

The vessel was of the common U form, and its capacity repeatedly determined from its resistance when filled with a concentrated NaCl solution. The acid, which we obtained through the kindness of Mr. F. W. Edwards of the Chemical Laboratory, was Baker & Adamson's strictly chemically pure H_2SO_4 of 1.84 spec. grav.

We give in the following tables the data of a number of our solutions sufficient to show the results obtained. In the first column the temperature is given; in the second, the actual resistance of the liquid; in the third, the specific conductivity. These values have to be multiplied by 10^{-12}. In the fourth column we find the molecular volume or molecular domain, *i.e.* the volume occupied by $\frac{1}{2}$ gram-equivalent of H_2SO_4 expressed in cubic centimeters; finally, in the fifth column the molecular conductivity, the product of molecular volume into specific conductivity.

TABLE I.

97 % H_2SO_4. Sp. Gr. = 1.841 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
2°.8 C.	433.0 ohms	67.45×10^{-12}	27.29	1.83×10^{-12}
8°.0	370.0	78.93	27.36	2.16
12°.9	321.0	90.98	27.43	2.50
22°.5	248.0	117.80	27.56	3.25
29°.0	212.5	137.41	27.65	3.80
17°.5	282.0	103.61	27.50	2.85

TABLE II.

93.05 % H_2SO_4. Sp. Gr. = 1.834 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
2°.5 C.	426.0 ohms	68.56×10^{-12}	28.56	1.96×13^{-12}
6°.4	377.0	76.47	28.61	2.22
12°.1	317.0	92.13	28.69	2.64
16°.7	278.0	105.06	28.76	3.02
21°.4	243.0	120.20	28.83	3.46
28°.3	202.8	144.00	28.94	4.17

TABLE III.

91 % H_2SO_4. Sp. Gr. = 1.825 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.6 C.	470.0 ohms	62.14×10^{-12}	29.31	1.82×10^{-12}
6°.4	385.0	75.85	29.40	2.23
12°.3	320.0	91.27	29.48	2.69
17°.0	279.0	104.7	29.55	3.09
22°.9	237.0	123.2	29.64	3.65
28°.8	202.0	144.6	29.73	4.30
23°.2	233.0	125.4	29.65	3.72

TABLE IV.

88.6 % H_2SO_4. Sp. Gr. = 1.812 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
1°.0 C.	505.0 ohms.	57.83×10^{-12}	30.33	1.75×10^{-12}
6°.0	422.0	69.21	30.41	2.10
11°.0	352.0	82.97	30.49	2.53
17°.0	293.0	99.67	30.58	3.05
21°.8	253.0	115.4	30.66	3.54
29°.2	204.6	142.6	30.77	4.39

TABLE V.

86.55 % H_2SO_4. Sp. Gr. = 1.798 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	552.0 ohms.	51.51×10^{-12}	31.26	1.61×10^{-12}
3°.8	480.0	59.24	31.32	1.85
8°.9	390.5	72.82	31.41	2.29
14°.6	319.7	88.95	31.53	2.80
19°.1	277.0	102.66	31.59	3.24
23°.3	242.0	117.51	31.65	3.72
29°.3	205.0	138.72	31.75	4.40

TABLE VI.

85.7 % H_2SO_4. Sp. Gr. = 1.790 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	572.0 ohms.	49.72×10^{-12}	31.71	1.58×10^{-12}
8°.0	421.0	67.55	31.85	2.15
15°.5	319.0	89.11	31.98	2.85
23°.0	249.0	114.21	32.10	3.67

TABLE VII.

84.5 % H_2SO_4. Sp. Gr. = 1.780 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	591.0 ohms.	48.12×10^{-12}	32.34	1.56×10^{-12}
5°.9	468.0	60.76	32.44	1.97
11°.8	367.0	77.49	32.54	2.52
17°.4	301.5	94.32	32.64	3.08
24°.0	242.5	117.27	32.75	3.84
30°.5	199.0	142.90	32.86	4.70

TABLE VIII.

80.75 % H_2SO_4. Sp. Gr. = 1.741 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	487.0 ohms.	58.39×10^{-12}	34.60	2.02×10^{-12}
6°.0	404.0	70.39	34.71	2.44
10°.0	345.0	82.43	34.78	2.87
15°.5	286.0	99.43	34.88	3.47
20°.0	248.0	114.70	34.97	4.01
24°.9	214.0	132.89	35.06	4.66
30°.3	184.0	154.55	35.16	5.43

TABLE IX.

78.6% H_2SO_4. Sp. Gr. = 1.717 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	417.0 ohms.	68.20×10^{-12}	36.02	2.45×10^{-12}
5°.8	342.3	83.05	36.13	3.00
10°.7	289.0	98.39	36.22	3.56
14°.8	253.0	112.40	36.30	4.08
20°.1	216.0	131.66	36.40	4.79
24°.4	193.0	147.34	36.48	5.37
29°.8	167.0	170.28	36.53	6.23

TABLE X.

76.2% H_2SO_4. Sp. Gr. = 1.689 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	349.0 ohms	81.48×10^{-12}	37.80	3.08×10^{-12}
5°.7	297.0	95.75	37.92	3.63
10°.0	256.5	110.87	38.00	4.21
14°.9	221.0	128.67	38.10	4.90
19°.7	193.0	147.34	38.20	5.63
24°.3	170.0	167.28	38.29	6.41
29°.0	151.0	188.33	38.39	7.23

TABLE XI.

73.88% H_2SO_4. Sp. Gr. = 1.663 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	295.0 ohms	96.40×10^{-12}	39.57	3.81×10^{-12}
5°.3	252.0	112.84	39.69	4.48
10°.8	214.8	132.39	39.80	5.27
15°.3	189.0	150.46	39.90	6.00
19°.3	168.5	168.77	39.99	6.75
24°.1	150.0	189.58	40.09	7.60
30°.5	129.0	220.45	40.22	8.87

From the tables we platted for each solution the temperatures and the molecular conductivity, and determined from the curves the molecular conductivity of each at the temperatures 0°, 10°, 18°, 25°. By calculation we found, moreover, the molecular volume for each solution at those temperatures. The following table gives the results.

No.	0°		10°	
	Mol. vol.	Mol. cond.	Mol. vol.	Mol. cond.
1	27.25	1.66×10^{-12}	27.39	2.29×10^{-12}
2	28.52	1.80	28.67	2.48
3	29.30	1.78	29.46	2.50
4	30.31	1.69	30.48	2.44
5	31.26	1.61	31.43	2.39
6	31.71	1.58	31.89	2.33
7	32.34	1.56	32.50	2.35
8	34.60	2.02	34.78	2.87
9	36.02	2.46	36.21	3.49
10	37.80	3.08	38.00	4.21
11	39.57	3.82	39.79	5.14

No.	18°		25°	
	Mol. vol.	Mol. cond.	Mol. vol.	Mol. cond.
1	27.50	2.88×10^{-12}	27.59	3.46×10^{-12}
2	28.78	3.14	28.88	3.83
3	29.57	3.19	29.67	3.88
4	30.60	3.15	30.72	3.90
5	31.58	3.14	31.67	3.92
6	32.03	3.12	32.14	3.90
7	32.65	3.14	32.77	3.97
8	34.93	3.77	35.06	4.68
9	36.36	4.51	36.49	5.47
10	38.16	5.37	38.31	6.51
11	39.97	6.47	40.11	7.77

Platting four curves, for 0°, 10°, 18°, and 25° respectively, taking the percentages of the solution as abscissae and the molecular conductivities as ordinates, we find that the minimum does not correspond to the same concentration, as was given by Bouty.[1] But in platting the molecular volume,

[1] Comptes Rendus, 108, p. 394, 1889.

instead of the percentage, we find that all four curves show a minimum of conductivity for the same molecular volume, *i.e.* 32.1. *Thus it is not the concentration but the molecular volume which determines the conductivity of the acid.*

The latter four curves are shown in Fig. 2. There is a very slight discrepancy between the fourth and fifth solutions, owing to the fact that the

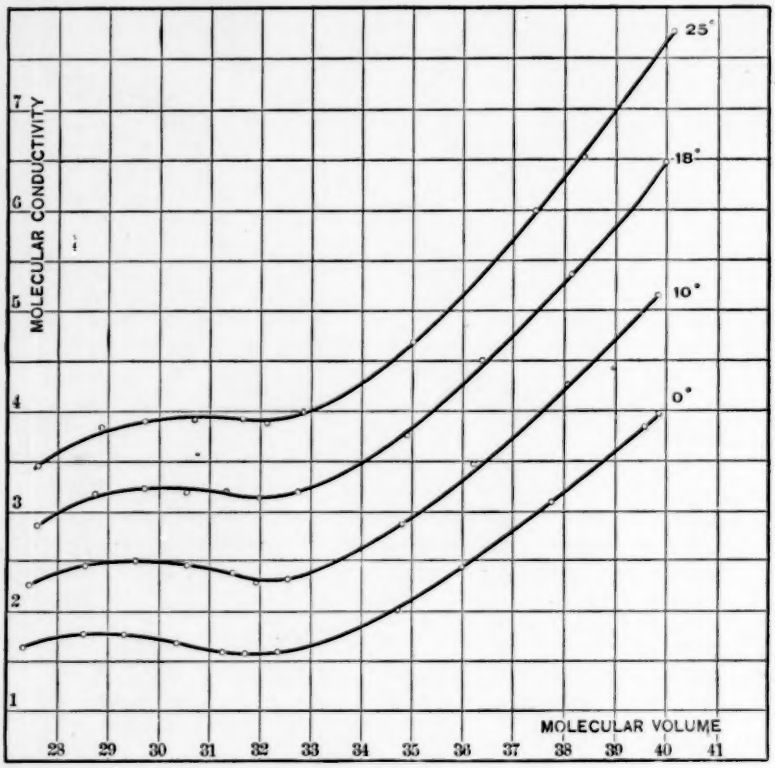

Fig. 2.

first four solutions were taken from a different bottle from that for the rest. But it is so small, in fact, as not to influence the result in the least.

Temperature coefficient.

In the following we give the first temperature coefficient for the different solutions worked out for the formula: —

$$\mu_t = \mu_{18}\{1 + \alpha(t_t - t_{18}) + \beta(t_t - t_{18})^2\}.$$

It is apparent that the temperature coefficient is the larger, the smaller the conductivity, a result already found by F. Kohlrausch and others. As to the second coefficient, we could not obtain regular values, due to the degree of accuracy in our method. It surely becomes smaller with increasing dilution, and varies from 0.00039 to 0.00016, and is always positive.

No.	1	2	3	4	5	6
α	0.0271	0.0291	0.0294	0.0315	0.0326	0.0338

No.	7	8	9	10	11	
α	0.0346	0.0321	0.0295	0.0290	0.0273	

Electrolytic Properties of the Crystallized Hydrate of Sulphuric Acid.

Since we obtained from one of the solutions crystals of $H_2SO_4 + H_2O$, we thought it worth while to determine its conductivity, since that has to our knowledge not been done before. From the experiments of W. Kohlrausch, Bouty, Poincaré and Graetz we know that the electrolytes conduct electricity when in a solid state and that the conductivity of some increases very rapidly near the melting-point. In some cases it becomes at this temperature equal to the conductivity of the liquid, while in other cases there seems to be a sudden change with liquefaction. Though these experiments are of the greatest importance for our knowledge of the molecular structure of the salts, they do not agree satisfactorily for the salts investigated, which all melt at a high temperature.[1]

Our measurements were taken without difficulty, the crystals melting at 7°.5 C., and the electrolytic properties are very characteristic. W. Kohlrausch[2] found that the conductivity of the crystallized acid $SO_3 + H_2SO_4$ was extremely small, and varied according to the way in which they crystallized. He attributed the remaining conductivity to enclosed liquid particles.

The salt $H_2O + H_2SO_4$ shows entirely different properties. We crystallized the same repeatedly, and obtained in some cases microscopical crystals (after having undercooled the liquid), in other cases crystals 2 to 4 cm. long. The resistance was always the same at the same temperature, showing clearly that the conductivity is not due to enclosed liquid particles, but is characteristic for the solid acid.

[1] Graetz, Wied. Ann., Vol. 40, p. 18, 1890. [2] Wied. Ann., Vol. 17, p. 80, 1882.

In the following table is given one series of observations, in which we calculated only the specific conductivity. The second table gives the measurements of the same solution in the liquid state.

CRYSTALS.

Temp.	Res.	Sp. cond.
−20°.0 C.	34000 ohms	0.846×10^{-12}
−15°.0	25000	1.147
− 8°.0	16200	1.755
∓ 0°.0	8200	3.47
5°.0	3530	8.06
7°.2	1514	18.78
7°.5	1000	28.44

LIQUID.

Temp.	Res.	Sp. cond.
0°.0 C.	585 ohms	48.61×10^{-12}
4°.8	481	59.12
9°.5	402	70.74
11°.0	376	75.63

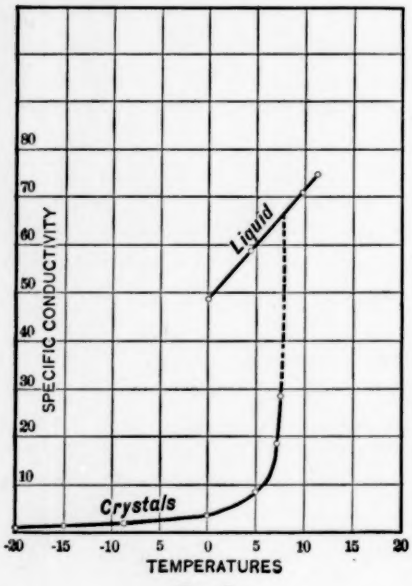

Fig. 3.

Platting the temperature and the specific conductivity, we see that the latter increases first slowly, but more rapidly the higher the temperature. Between 0° and 7°.5 this increase is enormous, but the conductivity of the crystallized acid does not reach that of the liquid. It reaches only the value 28.44 at 7°.5 while that conductivity of the liquid is 65.4. The last point for the crystals has been computed from the curve drawn with the resistances and the temperature as coördinates.

This increase of the conductivity, while the change from the solid to the liquid state takes place, seems to stand in a certain relation to the

energy taken up by the acid during liquefaction. In the curves the dotted line represents this increase.

This result does not agree with Fonssereau's,[1] who found the conductivity of the solid salts at the melting-point a thousand times smaller than that of the liquid. It agrees much better with Graetz's observations, though there is a slight sudden increase at the melting-point, while he finds no such step. In fact, a difference of only 1° C. would be sufficient to make one curve reach the other.

The sudden change of the temperature coefficient is very characteristic, and we see also that such a change does not take place when we undercool the solution.

[1] Comptes Rendus, 98, p. 1325, 1889.

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NEW BOOKS.

Grundzüge der Mathematischen Chemie, Energetik der Chemischen Erscheinungen. Von G. HELM. Leipzig, W. Engelmann, 1894.

At a time like the present, when both physics and chemistry are obscured by so many unnecessary hypotheses, every attempt to show the power and simplicity of general methods is very welcome. Although the general methods may themselves rest on certain assumptions, the fact that these assumptions are few, simple, and easily kept in mind is a great advantage. For one of the greatest difficulties the student has to encounter is that of remembering, often, indeed, of discovering, the hypotheses upon which the correctness of a theoretical result depends. The usefulness of thermodynamic, or energetic, methods has nowhere been greater than in the borderland between physics and chemistry. We are, however, inclined to think that pure physics may profit quite as much as physical chemistry from greater attention to the part which energy and its transformations play in natural phenomena, and that the greater advances in this direction made by physical chemistry are due rather to freedom from a long history of special hypotheses than to any intrinsic difference between the two fields.

The work before us is an attempt to give a concise and consistent treatment, based, as far as possible, only on the two laws of thermodynamics, of some of the recent advances in theoretical chemistry. It is divided into four parts, which treat *Energy*, *Entropy*, *Chemical Intensity*, and *The Degree of Freedom of Chemical Phenomena.*

Part I. contains a very good treatment of the law of the conservation of energy as applied to thermo-chemistry; in other words, of the proposition that the variation of the internal energy of a system depends only on the initial and final states of the system. We have two faults to find with Part I. The first is the failure to define temperature carefully. A satisfactory treatment of temperature must of course be left till the second law has been introduced, but we feel, especially at p. 14, that the meaning of "Celsius temperature" needs a precise definition. The second fault is a lack of clearness in the definition of molecular weight. It is, in our opinion, altogether a mistake to say (p. 15) that by the "law" of Avogadro the gas constant R in the equation $pv = RT$ is the same for one-gram molecule for all gases. This so-called law is simply our only defini-

tion of the molecular weights of gases, and our chemical molecular symbols are not independent of it, but deduced from it. The mere fact that our molecular weights so obtained are in general very simply related to the compositions of the gases in question, does not make us the less dependent on the fundamental definition in originally finding them.

Part II., headed *Entropy*, treats the second law of thermodynamics, and applies it to several problems, especially such as come under the head of Clapeynon's equation. This part seems to us the least satisfactory in the book, and we doubt whether the student who is not already familiar with the equation

$$\int \frac{dQ}{T} = 0$$

will make much out of what is here given on that subject. The greatest care and precision are necessary if the meaning of entropy and of the expression $\int \frac{dQ}{T}$ is to be understood, and this precision of statement is often lacking. One wishes that the meaning of reversibility might be as well set forth as in that delightful book of M. Duhem, the *Introduction à la Mécanique Chimique*. It is perhaps carping to object to the statement that the efficiency of an irreversible engine is always less than that of a reversible one, but we have never seen a satisfying proof of that proposition. M. Bertrand's remark seems just when he says in Chapter XII. of his *Thermodynamique*, "Je serai très bref sur les cycles irréversibles; les démonstrations et les énoncés mêmes de leurs propriétés me paraissent jusqu'ici manquer de rigeur et de précision." There is, to be sure, an air of originality about the whole treatment, and this in itself is attractive, but the result seems to us less clear and simple than more ordinary methods. After this unsatisfactory section on entropy comes a short but very good introduction to free energy, the thermodynamic potential, and Gibbs's potentials, here called "chemical intensities." Most of the rest of Part II. is given up to applications of the foregoing principles to cases of equilibrium between two phases, — evaporation, allotropic changes, etc., — and to the theory of the reversible galvanic cell. In this last the author again fails to discuss reversibility, the question of the irreversible Joule heat not being mentioned. There follows an interesting paragraph on the relation of chemical intensity and electromotive force, and Part II. closes with a few pages on the conductivity of electrolytes.

Part III. begins with a section on the general properties of the chemical intensity, in which Gibbs is followed. The remainder of this most interesting division of the book considers a number of subjects by means of the chemical intensity. Among them are chemical equilibrium, osmotic pres-

sure, and diffusion, which may serve to indicate the wide range covered by Gibbs's theory.

Part IV. deals with the phase rule, of course from Gibbs's standpoint.

Throughout the work numerical examples are introduced very judiciously to illustrate the theoretical results obtained.

To the student who is not already familiar with the elements of thermodynamics, and to some degree with free energy or the thermodynamic potential, the book will be hard reading. But the more advanced student will find it very useful as a short statement of a theory which he would otherwise have to dig out of many scattered and often obscure papers. The general impression left in the reader's mind is that so good a book ought to have been better written; but the faults are faults of detail, while the merits are those of unity and generality. We cordially recommend this work to all who are interested in physical chemistry, and we hope that this first example may find imitators in America, as it is sure to do in Europe.

EDGAR BUCKINGHAM.

BRYN MAWR, May 7th, 1895.

Ostwald's Klassiker der Exacten Wissenschaften.[1] 8vo. In Leinen Gebunden. Leipzig, Wilhelm Engelmann, 1894.

It is often difficult to realize that knowledge regarding many of the familiar facts of to-day has in many cases had a slow and laborious growth. Conceptions which we at the present time accept without a thought as to their origin have startled the scientific world at their announcement, and have set at work many a patient observer who, by his labors, has contributed no unimportant share to the world's present store of knowledge.

In a most charming series of little volumes, entitled *Ostwald's Klassiker der Exacten Wissenschaften*, Professor Ostwald of Leipzig has republished the original papers of early investigators along different scientific lines, and has thus brought these truly classic pieces of scientific literature within the reach of all. The interest felt in these papers is increased when one realizes that from these as a germ much of the present science has grown. Throughout this series of works the groping of the investigator

[1] No. 52. Über die Kräfte der Electricität bei der Muskelbewegung. Aloisius Galvani, 1791.

No. 56. Die Gesetze der Ueberkältung und Gefrierpunktserniedrigung. Sir Charles Blagden, 1788.

No. 57. Abhandlungen über Thermometrie, von Fahrenheit, Réaumur, and Celsius. 1724–1730–1733–1742.

No. 59. Otto von Guericke's neue Magdeburgische Versuche über den leeren Raum. 1672.

is always apparent. If the reader occasionally marvels that a wrong conclusion was drawn from facts observed, or that phenomena apparently so patent escaped detection, he is quite as frequently delighted at the originality of the ideas, and the brilliancy of the conceptions, which seem now almost to have come by intuition. In all, there have been up to the present time about sixty of these little volumes published. The four mentioned below may serve to give some idea of the value of the series.

In No. 52 is contained the account by Galvani of his experiments with electricity in producing the muscular contractions in a frog's legs. At first statical electricity alone was employed, and the effects of insulators and conductors, of positive and negative electricity, were carefully investigated. Galvani's next step was to examine the effects produced by atmospheric electricity. A pointed rod, carefully insulated from the roof, was placed upon the house, and securely grounded by being connected with the water in a well. The prepared frog's legs were placed across a break in this rod, and violent contractions were observed whenever a flash of lightning was seen. That Galvani was aware of the danger attending this experiment, and of the fatal result to Richmann of a precisely similar experiment in 1753, is evident from his remark that "a careful and intelligent arrangement in this experiment must be observed." Galvani's later and more important experiments consisted in effecting the muscular contractions by the difference of potential produced by the contact of two different metals. These contractions occurred whenever the metal hook, which passed through the spinal column of the frog, touched the metal plate upon which the frog's legs rested. These phenomena Galvani attributed to the electricity resident in the frog. "It is easy, however," he says, "to be deceived by experiment, and to imagine that to be seen and found, which one wishes to see and find." Reil of Halle, and later Volta, argued that "the seat of the irritation is in the metals, that of the irritability is in the organism." Thus early began the discussion as to the seat of the electromotive force, which even to-day is not settled.

No. 56 of the *Klassiker* contains an account of two important researches carried on by Sir Charles Blagden, about the year 1788. The first is on the supercooling of water; the second is the more famous one on the depression of the freezing-point of liquids due to dissolved substances. Both researches are models of logical experimentation, and are, for their time, very accurate. In the first, the author repeated earlier experiments on supercooling, and studied the effects of various substances — salts and gases in solution, substances in suspension, etc. — in increasing or decreasing the amount of possible supercooling. The second paper contains the record of experiments which established the law that the depression of the freezing-point is proportional to the amount of the dis-

solved substance. Blagden's work remained unnoticed, and the same law was rediscovered by Rüdorff after a lapse of nearly eighty years. The history of these investigations, carried out first by Blagden, later by Rüdorff, Coppet, and Raoult, forms one of the most interesting chapters of modern chemistry, and leads up to the important generalizations of van't Hoff, regarding the nature of dissolved substances.

No. 57 of this series contains the original papers in which Fahrenheit, Réaumur, and Celsius published their discoveries regarding the proper construction and calibration of thermometers. Fahrenheit, according to his own statement, was led to construct a thermometer through the announcement by Amontons that water always boils at the same temperature. Wishing himself to observe this "beautiful phenomenon," Fahrenheit constructed the first mercury thermometer, and fixed thereto the arbitrary scale which now bears his name, and which contained three fixed points. For the zero of this scale he chose the point of "most intense cold," which was the temperature obtained by mixing water, ice, and sal ammoniac or common salt. The second fixed point was determined as the temperature of melting ice, which was 32 on Fahrenheit's arbitrary scale, and the third as the temperature of a healthy person, which temperature fell at 96. That the temperature of boiling water fell at 212, was purely accidental. It is strange indeed that Fahrenheit nowhere speaks of the proportions of his freezing mixture, whereby his zero was determined, and also equally strange that he should not have chosen the boiling-point of water as one fixed point, inasmuch as his attention had been especially directed to the constancy of this temperature.

Réaumur, who appears to have been ignorant of Fahrenheit's work, thought mercury to have a coefficient of expansion too small to permit of its use in a thermometer, and so chose alcohol as his thermometric substance. To obtain a sufficiently high sensibility he was obliged to use a bulb four and one-half inches in diameter, although, as he himself foresaw, so large a bulb could not indicate rapid changes of temperature. The principle employed by Réaumur in graduating his scale was radically different from that used by Fahrenheit. Réaumur assumed that only one fixed point was necessary, and chose for this the temperature of melting ice. He then determined the volume of the bulb, and so graduated his tube that each division or degree represented one one-thousandth of the entire volume of the alcohol in the bulb, when at the temperature of melting ice. As the alcohol expanded when heated, the actual increase in volume was then read off on the stem. Under these circumstances, the temperature of boiling water was indicated by the point 80 on his thermometer, although it is clearly evident that the temperature of the thermometer was not that of the boiling water in which it was placed.

Celsius, whose work followed closely upon that of Réaumur, chose the two fixed points now used — the melting-point of ice, and the boiling-point of water — and divides this interval into one hundred equal parts. He, however, mentions the fact, also referred to by Fahrenheit, that the temperature of boiling water varies with the pressure of the air, and suggests a constant barometric height at which this temperature should be taken. An important feature of Celsius' work was the introduction of the 100-degree scale, although such a scale had in all probability been suggested by du Crest in France. It is worthy of notice that Celsius, in his original paper, called the temperature of boiling water 0, and that of melting ice 100. Not until this paper appeared in the eleventh volume of the Proceedings of the Swedish Academy, do we find these figures reversed, and the scale given in the familiar form in which it is universally used.

Otto von Guericke, in the fifty-ninth volume of this series, writes of the properties and pressure of the atmosphere, and later describes the air pump devised by him, and gives the details of his many experiments with this remarkable piece of apparatus. After demonstrating the impossibility of exhausting the air from a barrel, owing to the porosity of the wood, von Guericke substituted a thin copper sphere for the barrel, only to find the sphere crushed by the pressure of the air. Later followed the construction of the large hemispheres, which, when exhausted, twenty-four horses were not able to pull apart. That the air has weight, he proved by weighing a receiver filled with air, and then empty, and noticing the diminished weight in the latter case. The pressure of the air due to its own weight, he argued, must diminish as one ascends a mountain, and he proved this to be so. The abhorrence which nature was supposed to possess toward a vacuum he showed to be identical with the atmospheric pressure. Furthermore, he argued, this pressure of the air could be balanced by an equal pressure, and proved his statement by exhausting the air from the upper end of a long closed tube, the lower end of which was open, and under the surface of water. The water rose in the tube, until, as he explained, the pressures at the surface of the water in the reservoir, outside and inside the tube, were equal. In his study of this column of water, von Guericke noticed its rise and fall with the varying pressure of the air, and placed within the tube a little floating figure, whose finger pointed to a scale on the outside of the tube, indicating the atmospheric pressure. On one occasion, as the figure sank far below his usual position, indeed, even below the scale on the tube, von Guericke announced to his friends that a storm was approaching. In less than two hours the storm broke, and thus was fulfilled probably the first weather prediction based upon meteorological instruments. Von Guericke's original air pump, as well as the colossal Magdeburg hemispheres, are now guarded as among the most valued treasures in the Berlin Physical Laboratory.

BENJ. W. SNOW.

Popular Scientific Lectures. By ERNST MACH, translated by THOMAS J. MCCORMACK. 8vo, pp. 313. Chicago, The Open Court Publishing Co., 1895.

This work is a translation of a series of lectures delivered by Professor Mach of Prague at various times between 1864 and 1894. The name Popular Scientific Lecture often conveys to the scientist the idea of dilettanteism, and the practice is condemned, and rightly, too, if the lecturer only brings before his audience a mass of details, interesting in themselves, but leaving in the minds of the hearers no one central idea. When done well, however, as in the present case, nothing but praise is the lecturer's due, and scientific inquiry is distinctly advanced. The book easily divides itself into two parts, the first seven lectures dealing with explanations of simple phenomena, and the last five lectures dealing with questions of a more philosophical and educational nature.

The first group of seven lectures belongs to the earlier period of Professor Mach's career. The first requisite of a lecture is that it shall impart information, but more important is it that the information so imparted shall cause the listener to think. The lecturer must choose from the mass of illustrations at hand those most explanatory, and must confine himself to a single line of thought. Judged in this way, these lectures are admirable. Professor Mach takes a few common, every-day phenomena, and in simple language leads his audience from the fact itself to the larger concepts that lie behind it, without their ever feeling that they are beyond their depth. Perhaps the best of all the group is the first one of this volume on "The Forms of Liquids." To the unthinking, he says, the most noticeable property of liquids is their want of form; but a discussion of the raindrop and the soap-film, in a simple and elementary but masterly way, leads to a very different conclusion. Then follow two lectures on Acoustics: viz. "The Fibers of Corti" and the "Causes of Harmony." Three lectures on Optics, under the headings "The Velocity of Light," "Why has Man Two Eyes?" and "On Symmetry," treat in a very elementary manner of some of our commonest observations, the simple explanation of which is not always easy even to one who has studied them. Mach shows that the pleasing effects of symmetry are due to the repetition of sensations; where symmetry does not produce such repetition, as in the passage from a major to a minor scale in music, this agreeableness is not experienced. The lecture on "The Fundamental Concepts of Electrostatics" is a good example of the possibility of putting in simple, untechnical language such difficult ideas as those contained in the measurement of current, electromotive force, capacity, etc., and in a manner, too, suited to the most non-mathematical person.

Perhaps the chief interest to a reader of this volume will lie in the last half of it. The lecture on "The Conservation of Energy" deals historically with the part which the principle of the impossibility of perpetual motion has played in the subject of mechanics, and the proof of the principle of the conservation of energy as derived from that subject. His statement of the results to be deduced from the fact that heat has a mechanical equivalent will repay careful reading. It does not follow that heat is not a substance, he says, and the idea that heat is a quantity is due entirely to historical connection. There is no doubt that much of the subject matter of dynamics has yet to be recast; the laws of Newton are not yet in their best possible form. The chapters on "The Economical Nature of Physical Inquiry," "Transformation and Adaptation in Scientific Thought," and "On the Principle of Comparison in Physics," treat in a clear and thoughtful way of those broader aspects and methods common to all scientific inquiry. The last address, "On Instruction in the Classics and the Sciences," is a forcible plea for the study of mathematics and the sciences; but it is a pity to see a man of the stamp of Professor Mach put forward some of the arguments which he does against the study of the classics. That much is to be said for a more general study of the sciences is true, but that this end should be gained by crying down the value and power of a classical education is to be deplored. His plea for less work in the preparatory schools, and a restriction of the number of subjects studied, is one that appeals strongly to us in this country also. "A single philological, a single historical, a single mathematical, a single scientific branch, pursued as common subjects of instruction for all pupils, are sufficient to accomplish all that is necessary for the intellectual development" (p. 290).

The translator deserves praise for the general excellence of his rendering in spite of a few evident traces of its being a translation. The publisher's work is all that could be desired.

A. Stanley Mackenzie.

Proceedings of the Electrical Society of Cornell University. Vol. II., 1894–5. 8vo, pp. 122. Ithaca, Andrus & Church, 1895.

The second volume of the Proceedings of the Electrical Society of Cornell University includes the following papers: Difference of Electrical Potential between Substances in Contact; Metals for Magnet Cores; Fuse Wire; Lightning Arresters; Mechanical Equipment of Power Stations; Some Points in Connection with the Modern Theory of Primary Batteries; A Method of Reducing Hysteresis Losses in Armature and C^2R Losses in the Field; Electricity and Mining; Electrical Resonance and Some Allied Phenomena; Alternating Current Motors; Metallic Conduction and the Influences which affect it.

Standard Methods in Physics and Electricity criticised, and a Test for Electric Meters proposed. By H. A. NABER. 8vo, pp. 114. London, George Tucker, 1894.

The volume before us is principally devoted to presenting the advantages of the Naber gas voltameter, for which the author makes the most extravagant claims. The useful applications claimed for the instrument extend to almost all branches of scientific and technical electricity, from the accurate measurement of current and electromotive force, both direct and alternating, to the determination of the form of an alternating current curve. Frequent references throughout the book to authorities show on the part of the author an extensive acquaintance with the literature of electricity. It is to be regretted that so little appreciation is shown of the value, in fact the necessity, of experiment. In spite of the claims made for the voltameter in question, no quantitative tests of its action are cited. Most readers will I think join with the reviewer in postponing a serious consideration of the contents of the book until the author's claims have received some experimental verification.

E. M.